INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE NINETY-NINTH GENERAL MEETING of the Institution of Petroleum Technologists was held on Tuesday, February 8, 1927, at the House of the Royal Society of Arts, John Street, Adelphi, London, W.C., Sir THOMAS H. HOLLAND, K.C.S.I., K.C.I.E., D.Sc. (President), occupying the Chair.

The Secretary read the list of members elected since the last meeting, as follows :—

Members.—David Donoghue, Ion Edeleanu, Willem A. J. M. van Waterschoot van der Gracht, Basil Rawdon Jackson, Gulian Lansing, Elias Moscovici, Edward Thomas Newton-Clare, Lajos Steiner.

Associate Members.—Thomas Raymond Anthony Bevan, Chester M. Guess, William Leighton Johnson, David Speirs Paul, Robert Neil Scott, John Martin Walsh.

Transference to Associate Member.—Robert Ernest Palmer.

Students.—Frank Ernest Lawrence Smith.

Transference to Associate.—Walter Cattrall.

The President announced that the Ninth Annual Dinner of the Institution would be held on Tuesday, December 6, 1927, instead of on Monday, November 7, as previously announced.

The question of the Students' Medal and Prize had been considered by a Special Committee, whose findings had been reviewed by the Council. Eight papers came under consideration during the past year, one of which was disqualified under the Rules owing to it being a joint paper. The Committee unanimously recommended that the Medal and Prize for the year be awarded to Mr. H. S. Garlick for his paper on "The Scottish Shale Oil Industry." Mr. Garlick was a runner-up for the Medal and Prize in the previous year, and was then awarded a special Prize by the Council. It was satisfactory to realise that Mr. Garlick's keenness in the work of the Students' Section remained unimpaired, and that he was able to contribute two further papers, one of which the Committee and Council now considered to be suitable for the Medal and Prize. The Committee called the attention of the Council to the fact that the papers generally were of a very high standard, and specially commended three : (1) by Mr. M. Ba-Yan on "Petroleum Refining in Burma" ; (2) by Mr. W. B. Rowntree on "The Essential Qualities of Various Petroleum Products" ; and (3) by

Mr. J. O. Tanner on the difficult subject of "Electrical Methods of Prospecting for Oil."

He now had another announcement to make which he knew the members of the Institution would receive with real pleasure, namely, that the Council had persuaded Mr. Alfred C. Adams to accept the office of President as from the following month. Mr. Adams was one of the original 29 members of the Institution, and it was through his careful guidance especially that the finances of the Institution had been so satisfactory from the beginning. The Institution had gradually expanded in its income and its activities without any sudden jumps, and without any kind of set-back. Mr. Adams' annual presentation of the accounts of the Institution had always been one of the satisfactory features of the year's proceedings. He had always been a very active member of the Council who took a keen interest in the work of the Institution, and he was quite sure that the members abroad, as well as those at home, would hear with great satisfaction that he had been persuaded to accept the office of President.

He also further desired to announce that, under the powers conferred upon them by the Bye-Laws, the Council had elected the following gentlemen to be Vice-Presidents for the ensuing year: Sir John Cargill, Lord Cowdray, Mr. Alexander Duckham, Mr. Arthur W. Eastlake, Dr. W. R. Ormandy and Mr. Robert Redwood.

The paper that was due to be read was one that the Institution were very fortunate indeed to receive. Probably if the new Institution of Fuel Technology had been active a few months earlier their own institution would not have had the privilege of hearing Dr. Lander's paper, which suggested to him that there was room in London for correlating the activities of institutions which dealt with subjects of a similar nature. He hoped that in future papers of that character would be read at joint meetings of more than one institution, instead of, as at present, at the meeting of their own Institution. At the same time the paper was one on which the Institution could make a special claim. The Fuel Research Station, which Dr. Lander would refer to frequently in his paper, was really born out of the mental working of the Royal Commission on Oil which was appointed, with characteristic forethought, by Mr. Winston Churchill in 1911 to prepare the Navy for a possible war. Out of that Royal Commission grew various by-products, one of which was the Institution, because it was at the Luncheons between the meetings of the Royal Commission that the idea was first discussed of forming an Institution of Petroleum Technologists. As a result Dr. Beilby, as he then was, began to develop the idea of the necessity of having some

institution in this country which would devote serious attention to the possibility of obtaining oil from coal. Out of that primary idea ultimately grew the important Research Station to deal with fuel questions, and Sir George Beilby, an old member of the Institution and a member of the Royal Commission on Oil Fuel, was its first Director. There was therefore a direct genetic connection between the Institution and the Fuel Research Station, and for that reason he hoped their friends in the Institution of Fuel Technology would not be jealous if the Institution of Petroleum Technologists had the privilege of hearing Dr. Lander's paper first. He was glad to see present at the meeting a number of visitors from other Institutions, and he personally welcomed Dr. Lander as an old colleague in Manchester.

The following paper was then read:—

The Production of Oil from Bituminous Coal. An Account of the Work of the Fuel Research Station.

By C. H. LANDER, D.Sc., M.Inst.C.E., M.I.Mech.E., F.Inst.P.

ALTHOUGH it is realised that the interests of the present audience lie mainly in the direction of oil production, it is desirable, before turning specifically to questions of oil production, to state briefly some of the objects which were in the minds of those who were responsible for the inception of the Fuel Research Board early in 1917.

In the first report presented to the Committee of the Privy Council for Scientific and Industrial Research it was pointed out that the field covered by fuel research is a very wide one, and embraces enquiries into the sources and qualities of both coal, oil shales, natural oil and natural gas, and peat; into the methods of preparation of other fuels from these natural raw materials, and also into the uses of all forms of fuel, both natural and manufactured, for the production of heat, light, and power. The ultimate aim in an organised enquiry of this nature must be regarded as the securing of greater health, comfort and convenience for the community, through the more economical use and the more scientific development of the natural resources of the Empire.

During the ten years which have elapsed since the presentation of this report these ideals have been constantly borne in mind and the work of promoting them, whether undertaken directly for the Board or by other bodies or individuals subsidised by the Department on the recommendation of the Board, has been directed down many different avenues, and has been concerned with most of the forms of raw material enumerated above. Although some of the paths investigated have necessarily led to a blank end, in

other cases the explorations have opened up very attractive fields, in which considerable progress has been made.

It has been pointed out on many occasions that the world's main natural source of energy is coal, the known deposits of which are many times greater than those of any other fuel which can be used in a raw or unmanufactured form. This general position is greatly intensified in the case of Great Britain where one type of fuel of considerable importance in our present form of civilisation does not exist at all in the natural state. If the present lines of development in the use of oil fuel are to continue it is obvious that at some time or other in the world's history oil will have to be obtained in large quantities from other than natural sources, and in view of the unfavourable position of these islands in regard to natural oil, it is important that Great Britain should be ahead of the whole world in the development of processes for the production of manufactured oil from fuel resources which do exist in the country.

The process of development can only take place gradually, and will be profoundly affected by the existence of large quantities of natural oil in other countries, since it is obvious that oil which has merely to be pumped from a well must usually be in a very favourable position as compared with oil produced from material which has first to be mined and then subjected to a manufacturing process, at any rate, if the oil so produced is looked upon as the main product of the process.

It is well known that manufactured oil can be obtained by a variety of processes, such, for instance, as the distillation of shale, the carbonisation or hydrogenation of coal, etc., the relative success of which will naturally depend largely upon local economic considerations. The shale industry has been developed in Scotland, but for various reasons is not in a very flourishing condition at the present time.

Such processes may be divided into two distinct categories according to whether they yield oil as the main product or as a by-product. It is obvious in the former case that unless the oil can be made at a phenomenally cheap rate undertakings will always be subjected to such disabilities as have re-acted from time to time in the shale oil industry, which has always been at the mercy of waves of depression coinciding with waves of increased activity and increased production of natural oilfields. Processes, on the other hand, in which oil is obtained as a by-product are in a more favourable position provided that they can be so worked that the profits on the main products are sufficiently great to mask the variations in price which must occur from time to time in oil.

It is for this reason, among others, that a considerable proportion of the activities of the Fuel Research Division have been devoted to investigations of high and low temperature carbonisation of coal with special reference to the possible better utilisation in the future of the 40 million tons of coal which is at the present time send in the domestic fires of our people.

It will be recognised that the economic difficulties of dealing with such large quantities of material must inevitably be very great since the raw material absorbed must be paid for at its full economic value, and the finished solid fuel has as a direct competitor the raw material from which it is made. This disability does not exist under more restricted conditions where the object of the process is the stepping up of cheap materials such as low grade slacks, etc., which have not borne their proper share of the original mining costs, and where there is in consequence a large margin between the price of the raw material and that of the manufactured product. The development of such processes is clearly of importance, but it is equally obvious that the fuel problem of this country will not be solved by such means alone, since the larger the operations involved the greater tendency there must be to the narrowing of the margin between the price at which the raw material can be obtained and the price at which the resultant fuel can be sold. The finished product, it must always be remembered, must compete with the very fuel whose high price was rendering it possible to sell the fines at a low price. Such considerations are, of course, only very broad, and in practice economic results would naturally be influenced in all kinds of directions by the local conditions of sources of supply, markets, and social habits.

In the development of any commercial process of carbonisation it is generally necessary that four distinct stages should be passed through :—

(1) The suggested method must be investigated under laboratory conditions where the varying factors involved can be subjected to close control and where relatively high accuracy of measurement can be obtained.

(2) The process is carried a stage further by erecting an intermediate scale unit with a view to obtaining further designing data for a still larger unit. In this stage the plant will probably deal with several cwts. a day.

(3) Making use of the information yielded in stage 2, a full scale unit must now be erected and tried out. The size of this unit would depend upon the type of plant, but might range between, say, 5 tons and 100 tons daily capacity.

It is essential that this unit should be capable of multiplication to the full size of commercial unit without any alteration in scale.

(4) A commercial battery consisting of several units similar to those developed in stage 3 would be erected in some favourable locality, and the economic possibilities of the system examined in actual practice, and, if necessary, tested by actual commercial audit.

The unfortunate history of the subject of low temperature carbonisation provides a clear example of the dangers of embarking upon commercial ventures without first fully investigating a process in all of the above stages, for it is plain that should any of the stages be omitted an element of gambling, in which the odds are frequently heavily against the promoters, must be involved. In the past much damage has been done to the cause of low temperature carbonisation by the omission of either stage 3 or 4, and plants of large size have been put up without a proper recognition of the factors involved, so that failure was almost inevitable. There are, however, several processes of low temperature carbonisation in which the work is being carried out on sound lines. Most of these may be said to have reached the end of stage 2; one or two are approaching the end of stage 3; none has yet reached the end of stage 4, where audited figures showing the actual profits made from a plant working under normal commercial conditions can be produced. It must not either be assumed that a single effort will necessarily be sufficient to give adequate information in any individual stage for carrying the experiments to the following stage with reasonable hopes of success. Prolonged investigation and the erection of many experimental plants may be called for.

The Fuel Research Station was erected and equipped with the definite object of carrying investigations of fuel treatment through all the necessary preliminary steps to success in stage 3; their subsequent economic success or failure can only be decided in conjunction with industry.

From what has already been said it will be gathered that the Fuel Research Station does not consist merely of a laboratory for small scale work; in fact, it has been the policy from time to time to make arrangements for some of the preliminary small scale work to be undertaken in the laboratories of universities and other institutions. The Fuel Research Station is in essence a full sized works in which provision has been made for the adequate investigation of apparatus on a full size scale, in which it has generally been found convenient so to design plants that their

throughput will be in the neighbourhood of 10 tons a day. In order that work might proceed uninterruptedly and at the same time without undue haste, arrangements were made with the South Metropolitan Gas Co., who provided the site at a peppercorn rent, for the sale of such surplus products—tar, ammonia, gas and coke—as might be available. The Station has grown rapidly to meet the needs of dealing with the many specific problems which have been introduced both at home and from all over the Empire, and it now contains full sized units ot various types of retorts for high temperature carbonisation, briquetting machinery, water-gas and waste heat recovery plants, steam boilers, gas producers, and gas and oil engines. A full scale washery comprising typical units and a Bergius plant capable of dealing with about 1 ton of coal a day, have recently been added to the equipment. Operations are conducted continuously, night and day, throughout the year, except that in August the experimental work is usually suspended in order to afford the necessary leave to the staff and at the same time put in hand alterations and renovations. It has always been considered essential that the utmost accuracy commensurate with the scale of the work should be attained, and the staff now has no difficulty in obtaining weight balances within about 1 per cent.

Upon the recommendation of Lord Haldane's Coal Conservation Committee, and recognising the importance of a thorough knowledge of the raw material available, a survey of the coal seams of the country has been instituted. The preliminary work of sampling and of subjecting the material to known chemical tests is conducted locally, but the final pronouncements as to the suitability of seams for the different industrial purposes are only made after full scale trials, which usually are undertaken at the Station.

When the Board included in their programme the problem of low temperature carbonisation a preliminary study of the existing information showed much of it to be inconsistent and therefore unreliable, and it became apparent that progress would not be made without a more systematic study of the general principles involved in carbonisation processes generally. Efforts were therefore first directed to the laboratory investigation of the problem, and a method of assay based upon that which had been used in the Scottish shale industry was investigated.

In the development of the assay apparatus, which was described in a paper by Gray and King (Fuel Research Board, Technical Paper No. 1, "The Assay of Coal for Carbonisation Purposes"), the following points were taken into account:—

(1) That while the scale on which carbonisation is carried out

should, from considerations of convenience and speed, be as small as possible, it must be sufficiently large to permit of the separate collection and direct measurement of all the products—tar, water, ammonia, gas and coke—so that a weight balance can be struck by which the whole operation may be checked and the qualities of the products ascertained by chemical or physical tests.

(2) That the primary products of carbonisation should be withdrawn from the zone of carbonisation at or near their temperature of formation, in order to minimise "cracking" or other secondary changes resulting from their contact with hot surfaces.

(3) That in order that the method may be widely applicable, it is desirable to avoid undue elaboration in the apparatus or the use of materials which are not available in any ordinary chemical laboratory.

A diagram of the assay apparatus is shown in Fig. 1, in which B is a silica tube heated in the furnace A, the liquid products being

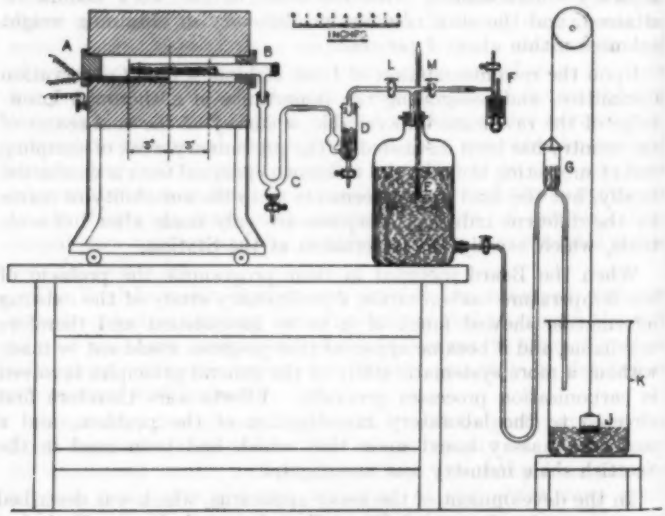


FIG. 1.

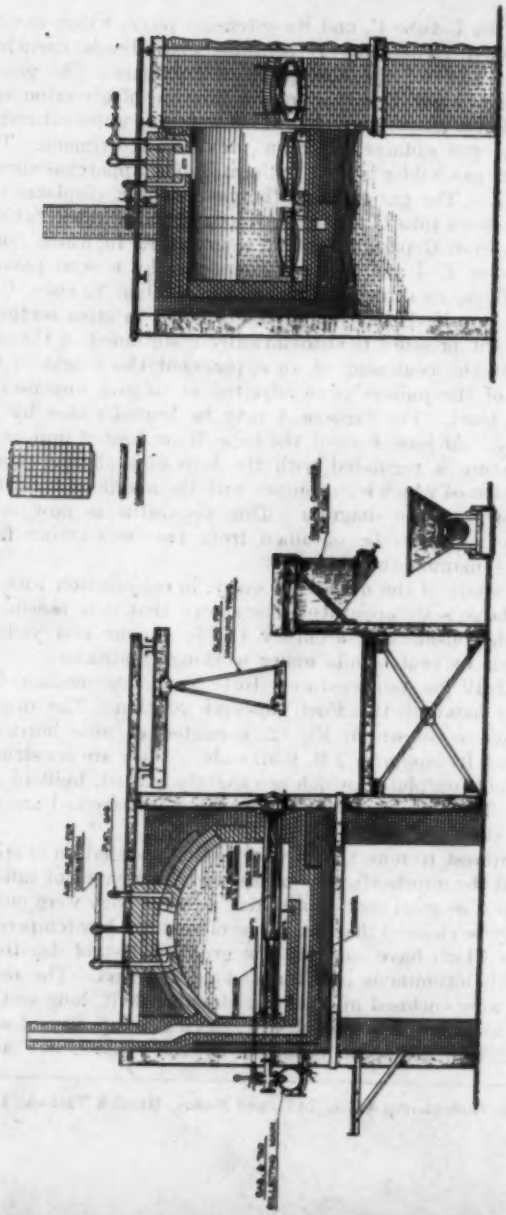
condensed in the U tube C, and its extension piece, which can be externally cooled. The tube D contains glass beads drenched with sulphuric acid for the absorption of ammonia. The gas is collected in the holder E, either over a mixture of glycerine and water, a solution of magnesium chloride in water, or water saturated with the coal gas obtained from a previous experiment. The pressure in the gas-holder is kept uniform by the apparatus shown at G, J and K. The gas entering the gas-holder E displaces the liquid, which flows into G through a piece of indiarubber tubing. The overflow from G passes into the reservoir K, in which floats the counterpoise J, J and G being connected by a cord passing over two pulleys, as shown. Thus as the level in K rises, G is lowered, and provided that E and K are equal in cross sectional area, a constant pressure is automatically maintained in the gas-holder E. At the beginning of an experiment the height of the vessel K or of the pulleys is so adjusted as to give any desired difference of level. The furnace A may be heated either by gas or electrically. At least 6 in. of the tube B are heated uniformly. The temperature is regulated with the help of a thermo-couple, the hot junction of which is in contact with the middle of the retort tube as shown in the diagram. This apparatus is now made commercially, and can be obtained from two well-known firms of apparatus manufacturers.*

A further study of the method of assay, in conjunction with the working of large scale apparatus, has shown that it is possible to forecast with considerable accuracy the behaviour and yield of different coals or coal blends under working conditions.

Early in 1919 low temperature retorts of an intermediate type were put in hand at the Fuel Research Station. The original setting, which is shown in Fig. 2, consisted of nine horizontal steel retorts, 9 ft. long and 2 ft. 6 in. wide. They are constructed of top and bottom plates, which are slightly curved, built of $\frac{3}{8}$ in. mild steel. The sides to which these plates are rivetted are 5 in. channels of standard section.

It is of interest to note that a part of this installation is still in use, and that the retorts after seven years working have not suffered, and are in just as good condition to-day as when they were put up. It may fairly be claimed that this is one of very few low temperature installations which have survived the gruelling test of day-to-day working with bituminous coal for so long a period. The retorts themselves were enclosed in a heating chamber 30 ft. long and 8 ft. wide, with an average height of 4 ft., having a capacity of about 960 cu. ft., less the space occupied by the retorts, say about

* Messrs. A. Gallenkamp & Co., Ltd., and Messrs. Baird & Tatlock, Ltd.



SETTING OF HORIZONTAL MILD STEEL RETORTS
FOR EXPERIMENTAL WORK ON LOW TEMPERATURE CARBONISATION OF COAL UP TO 650°C.

FIG. 2.

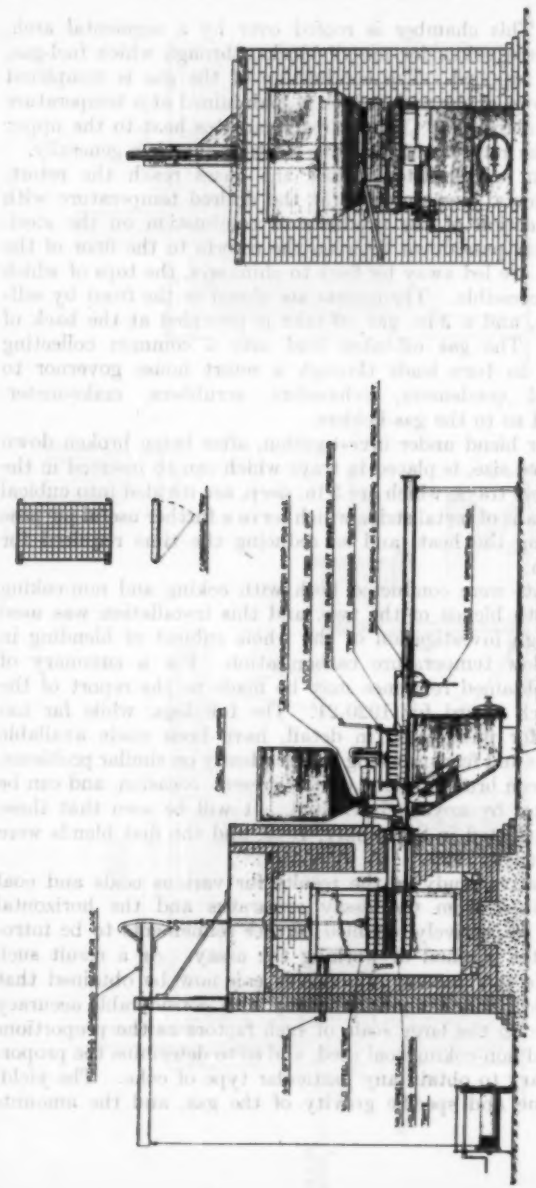
100 cu. ft. This chamber is roofed over by a segmental arch, pierced at three points for nostril blocks, through which fuel-gas, and air, are supplied. The combustion of the gas is completed under the crown of the arch, which is maintained at a temperature considerably above 600° C., and freely radiates heat to the upper surfaces of the retorts and into the heating chamber generally.

Combustion is completed before the gases reach the retort, so that the metal is maintained at the desired temperature with a minimum action of the products of combustion on the steel. These products pass down between the retorts to the floor of the chamber and are led away by flues to chimneys, the tops of which are readily accessible. The retorts are closed at the front by self-sealing doors, and a 3 in. gas off-take is provided at the back of each retort. The gas off-takes lead into a common collecting main, which in turn leads through a retort house governor to water cooled condensers, exhausters, scrubbers, make-meter, purifiers, and so to the gas-holders.

The coal or blend under investigation, after being broken down to the required size, is placed in trays which can be inserted in the retorts. These trays, which are 3 in. deep, are divided into cubical spaces by means of metal strips which serve a further useful purpose in distributing the heat, and so reducing the time required for carbonisation.

Experiments were conducted both with coking and non-coking coals and with blends of the two, and this installation was used for a thorough investigation of the whole subject of blending in relation to low temperature carbonisation. For a summary of the results obtained reference may be made to the report of the Fuel Research Board for 1920-21. The full logs, while far too voluminous for publication in detail, have been made available to individuals and firms working independently on similar problems. They have been brought along on the present occasion, and can be inspected later by anyone interested. It will be seen that these experiments started in September, 1919, and the first blends were tried in January, 1920.

A comparative study of the results for various coals and coal blends obtained from the assay apparatus and the horizontal steel retorts respectively, enabled further refinements to be introduced into the method of working the assay. As a result such correlation factors between the yields can now be obtained that it is possible in the assay to prophesy with considerable accuracy the influence on the large scale of such factors as the proportions of coking and non-coking coal used, and so to determine the proportions necessary to obtain any particular type of coke. The yield, calorific value and specific gravity of the gas, and the amounts



EXPERIMENTAL LOW TEMPERATURE RETORT FOR THE CONTINUOUS CARBONISATION OF COAL AT 600° C.

FIG. 3.

of ammonia and tar can also be predicted. The mean ration of yields $\frac{\text{Horizontal retorts}}{\text{Assay apparatus}}$ for the various products are approximately as follows:—

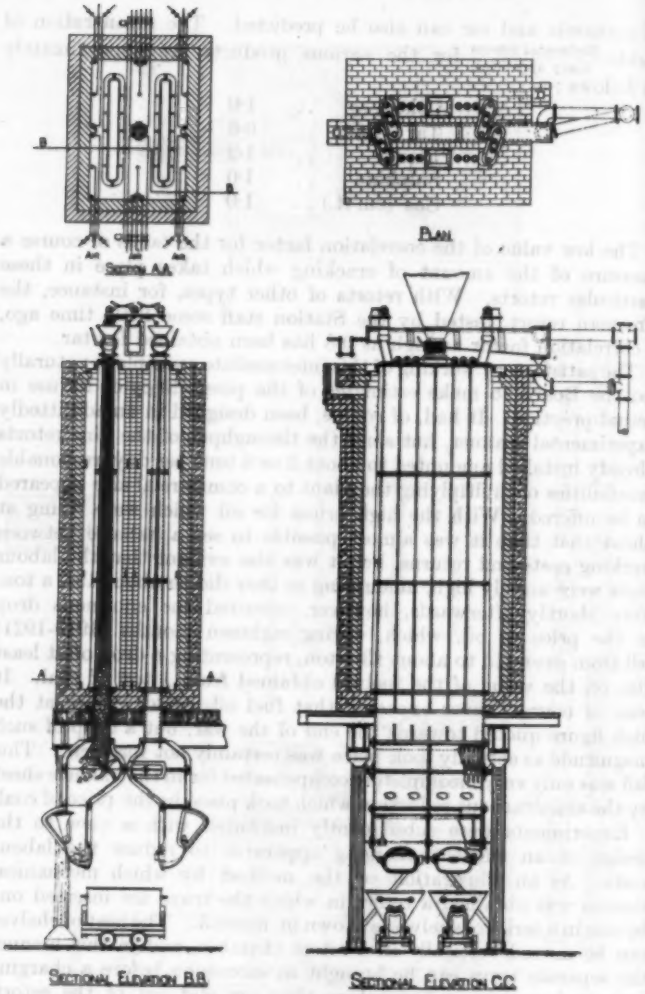
Coke	1·0
Tar	0·6
Liquor ..	1·2
Sulphate ..	1·0
Gas (cu. ft.) ..	1·0

The low value of the correlation factor for the tar is of course a measure of the amount of cracking which takes place in these particular retorts. With retorts of other types, for instance, the Freeman retort, tested by the Station staff some little time ago, a correlation factor as high as 0·8 has been obtained for tar.

The satisfactory working of this intermediate scale plant naturally led the Board to make estimates of the possibilities of its use in actual practice. It had, of course, been designed in an admittedly experimental manner, but since the throughput of the nine retorts already installed amounted to about 5 or 6 tons per day, reasonable possibilities of multiplying the plant to a commercial size appeared to be offered. With the high prices for oil which were ruling at about that time it was almost possible to see a balance between working costs and returns, but it was also evident that the labour costs were unduly high, amounting as they did to about 15s. a ton. Very shortly afterwards, however, occurred the enormous drop in the price of oil, which, during eighteen months (1919-1921) fell from over £15 to about £3 a ton, representing a drop of at least 10s. on the value of the fuel oil obtained from 1 ton of coal. It was, of course, never expected that fuel oil would remain at the high figure quoted towards the end of the war, but a drop of such magnitude as actually took place was certainly not foreseen. This fall was only very incompletely compensated for in the balance sheet by the simultaneous reduction which took place in the price of coal.

Experiments were subsequently instituted with a view to the design of an efficient charging apparatus to reduce the labour costs. As an illustration of the method by which mechanical success was obtained a retort in which the trays are inserted one by one in a series of shelves is shown in figure 3. The nest of shelves can be moved vertically in a retort chamber, and in this manner the separate trays can be brought in succession before a charging and discharging opening, where they are slid out of the retort, emptied, and returned with a fresh charge of coal quite mechanically.

Except for minor troubles which could, no doubt, have been overcome without much difficulty, this machine worked satisfactorily for a considerable period, but it very soon became apparent that


B
B
Air
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Air
SECTION A.A.
PLAN
A
A
SECTIONAL ELEVATION B.B.
SECTIONAL ELEVATION C.C.
SETTING OF CAST IRON RETORTS
FOR
LOW TEMPERATURE CARBONISATION
H.M. FUEL RESEARCH STATION, GREENWICH

FIG. 5.

although the labour costs had been reduced enormously the capital charges had at the same time gone up, and the net reduction in total charges was not sufficient to show a satisfactory balance sheet under the changed prices of the products.

These experiments were, therefore, discontinued for the time being in favour of investigations which appeared to hold out promise of more immediate progress; but it is interesting to note that the late Mr. Scott Moncrieff developed on the intermediate scale a plant whose principles were very similar to the one described. It is freely admitted that Mr. Moncrieff's plant was somewhat simpler than the one which had been constructed at the Station, but in the opinion of the speaker the capital costs even of this plant were still far too high. The economics of the original setting naturally only apply to costs, labour and material, as they obtain in this country, and with the raw material charged at the full wholesale price of household coal. In other circumstances, such for instance as obtain in some of the Dominions and Colonies, where cheap labour is to be had, and where there is a possibility also of obtaining relatively cheap material which can be stepped up so as to command a higher price, the speaker believes that certain promises would be offered by retorts similar to the original Station setting. At all events it is a thoroughly robust plant which can be relied upon for efficient working over long periods, producing a strong smokeless fuel from fine coals, together with adequate yields of by-products.

At this stage, as already stated, it was decided to approach the problem from a somewhat different angle, and to determine whether instead of designing an apparatus specifically for the purpose of overcoming the known disabilities, it might not rather be advisable to adopt a very simple type of plant and seek success by ringing the changes on the enormous number of alternative methods of working it. The long connection of the late Sir George Beilby with the Scottish shale industry led to the adoption of a type of retort based upon those used in that industry. It was further proposed to subject the raw material to some pre-treatment by which its properties might be rendered somewhat similar to those of the raw shale. The striking work of Sutcliffe and Evans in pre-briquetting coal under high pressures without an added binder appeared to offer some prospect of a solution, and briquettes supplied by Messrs. Sutcliffe Speakman were carbonised with a fair amount of success in the new plant, which is illustrated in figure 4. At the same time, it was thought that the range of coals which could be treated satisfactorily might be extended by adopting a slight modification of the Sutcliffe method, namely, by heating the coal to a temperature at which incipient fusion took place,

and briquetting it under much lower pressures. Two briquetting machines were installed for this purpose, the first being a standard Emperor press as used by Sutcliffe, and the second a new type of roll machine intended to produce higher pressures on the ovoid briquettes than could be obtained by the ordinary circular roll. The special feature of this new press lay in the fact that the rolls were polygonal. This machine was successful in producing briquettes under pressures estimated at about 2 tons per square inch. A long series of experiments was made in the laboratory in producing small pellets from heated coals, and it had appeared from these that a pressure of about 2 tons per square inch, together with a temperature of about 340° C., would give a thoroughly satisfactory briquette. When working on the full scale, however, it was found that long before this temperature was reached incipient decomposition set in, the evolution of vapours and gases at temperatures as low as 240° C. being sufficient to cause disintegration of the briquettes immediately the pressure under which they had been formed was released. The temperature which gave briquettes of maximum strength at a pressure of 2 tons per square inch was about 220° C., but even these briquettes were not sufficiently robust to stand the subsequent burden when they were carbonised. It may be remarked that this observation has led to further work in connection with the decomposition point of coal.

In the meantime the large setting which is known at the Station as setting "B" was used for the carbonisation of certain types of feebly coking coal such as those which are used by Mr. Maclaurin in his work. Such coals could be passed through the vertical retorts with ease, although the design of the extractor gear, a simple worm, tended to the production of large quantities of breeze. The same thing occurred when blends of coal were used, that is to say, the retorts could be worked, the gas yield was adequate, although the tar yield was poor, and the resultant coke contained a certain quantity of good smokeless fuel; and in spite of the fact that the breeze amounted in some cases to 30 or 40 per cent., the results generally were distinctly promising.

Two further settings of vertical retorts were subsequently put in hand in which the type of extractor gear, based on the well-known Woodall Duckham arrangement and designed in conjunction with this firm, was installed. At the same time the retorts were increased in size along the lines of the major axis. These retorts for convenience have been designated "D" and "E," and in what follows this nomenclature will be retained. A diagram of retorts "E" is given in Fig. 5, from which it may be seen that they consist of two iron boxes, 21 ft. high, of cross section, 6 ft. 6 in. by 7 in. at the top, and about 6 ft. 10 in. by

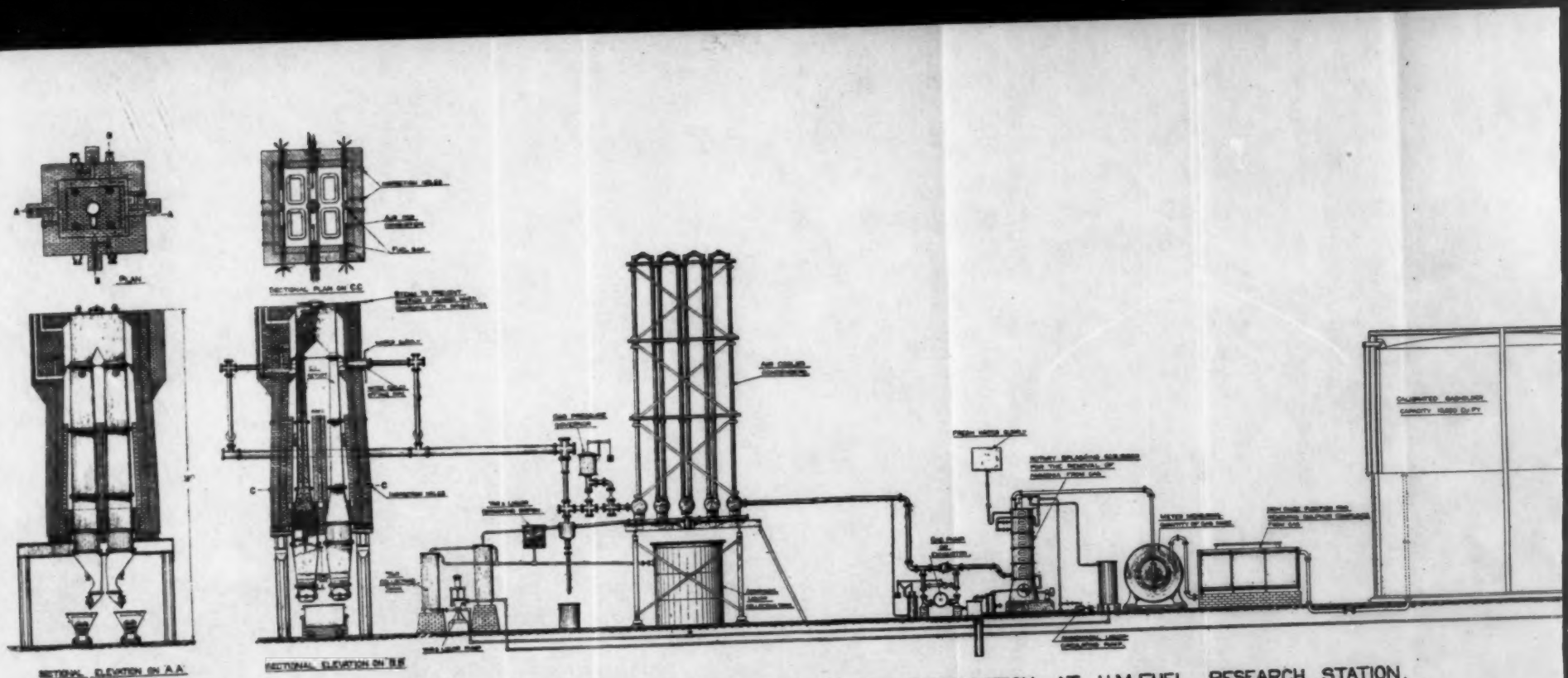
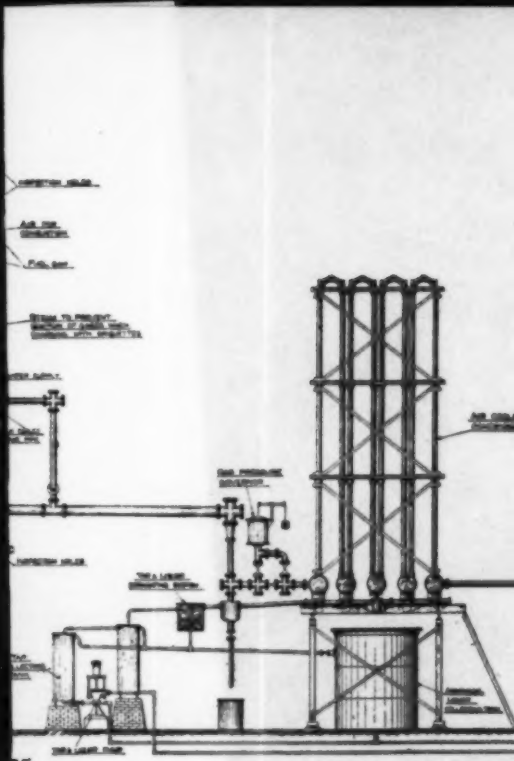
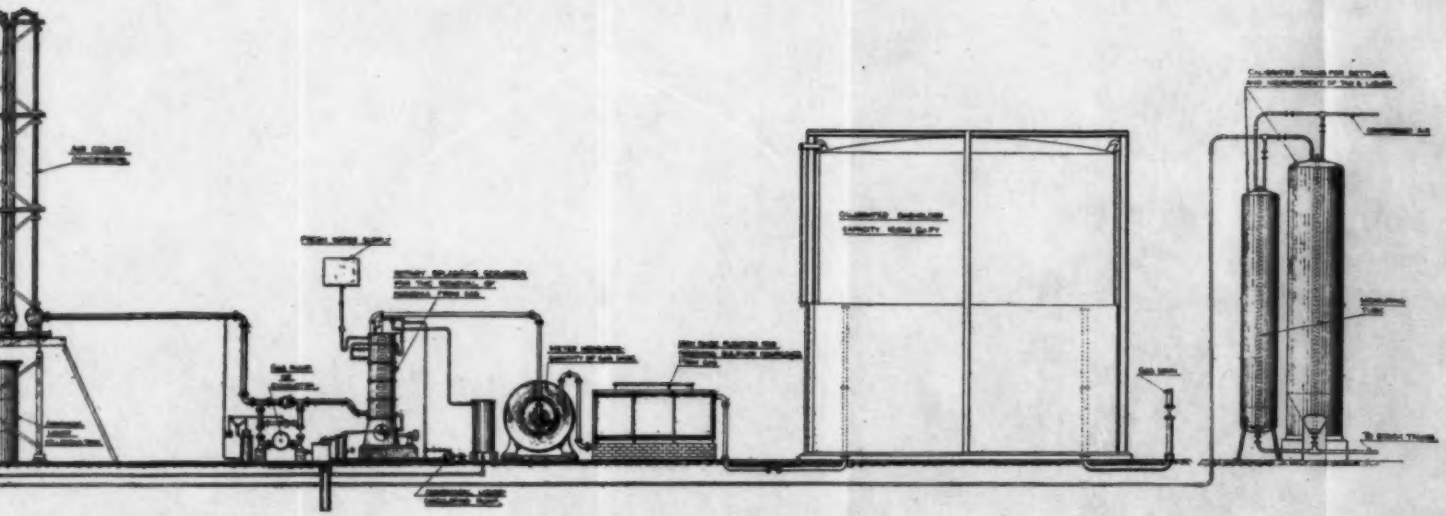


DIAGRAM OF CONTINUOUS LOW TEMPERATURE RETORT INSTALLATION AT H.M. FUEL RESEARCH STATION.

FIG. 4.



GRAM OF CONTINUOUS LOW TEMPERATURE



PERATURE RETORT INSTALLATION AT H.M. FUEL RESEARCH STATION.

FIG. 4.

11 in. at the bottom. Retorts "D" are similar in design, but are 3 in. narrower across the minor axis.

Retorts "D" were got to work first, but very soon gave trouble through distortion occurring at the temperature adopted, namely, 650° C. This distortion, though not great in amount, was sufficient to cause trouble in the working of the retorts since these were already too narrow, and an amount of distortion, small in itself, represented an appreciable proportion of the total width. They were, however, used for further work in connection with the carbonisation of non-coking and feebly-coking coals, with a view to the production of slack coke suitable for boiler firing.

Retorts "E" were much more successful. They were put under heat at Christmas, 1925, and the temperatures were gradually worked up, until in March, 1926, they stood at 625° C. beyond which it was considered inadvisable to push them. They were run at this level until December 27th, 1926, when they were cooled down for examination. A detailed account of the working of these retorts is in preparation, and will shortly be published, but it may be stated that it has been found possible to work them with sized coals ranging from feebly-coking to very strongly-coking; for instance, large quantities of Durham coal, from which the fines under ¾ in. have been screened, have been successfully worked through the retorts. Types of coal in nut form such as Dalton Main or Garforth Nuts are worked with the greatest facility, a slight amount of agglomeration taking place, and the resultant fuel being slightly larger than the raw material. A reduction in the amount of fines also occurs in the process. A certain amount of distortion has taken place, but up to the present this has not been sufficient to hamper in any degree the ease of working. At the time of writing this lecture they have been cooled down for inspection, but it is hoped that before it is delivered they may be under heat again and carbonisation proceeding regularly.

Retorts of this description may be worked either continuously or intermittently. When the former method is used the coal is kept in motion during the whole time it remains in the retort, and there is consequently a tendency for the discharge of fuel which has been so disturbed during its plastic state, that both its density and strength are seriously affected. On the other hand, with intermittent working the coal lies quiescent in the retort and the strength of the carbonised fuel is not impaired. Intermittent working, however, is much more severe on the metal retorts since there is a tendency for a rapid rise of temperature while the retorts are empty, followed by a sudden cooling down due to the incoming charge of coal. The coke discharge and

cooling boxes have to be made of sufficient size to deal with the entire contents of a retort. During the investigations it became apparent that a method of intermittent working in which the coal was dropped only a few feet at a time would present considerable advantages. The actual distance through which the coal is dropped in any one discharge must be modified according to the nature of the coal, but it has been found possible to deal with many varieties of material simply by the alteration of this factor.

The actual mode of procedure is somewhat as follows. The extractor gear, which can be controlled from the top of the retort, is set in motion, and sufficient coke is discharged into the cooling chamber to allow the level of the mass in the retort to fall about 3 ft. if the extraction takes place hourly, or 6 ft. if the extraction takes place once in two hours. The top level of the charge is gauged by pokers inserted through openings at the top of the retort. On the desired level being attained, the extractor gear is stopped and the space at the top explored with the poker to ensure that no scaffolding has occurred. The coal valve is then opened, and the vacant space filled up. The whole operation does not occupy longer than about three minutes, after which the retort can be left without any attention whatever until the time for the next charge and discharge comes round. The working of a bench of retorts would obviously be so arranged that no two retorts required charging simultaneously. The maximum use could thus be made of the labour employed at the top, and the total number of men required for operating a full scale bench would thus not be excessive. So far 1350 tons of coal have been put through these retorts, the products from which have been disposed of in the open market.

In accordance with the usual practice of the Station, the gas has been sold to the South Metropolitan Gas Co. Many samples of the tar have been supplied to outside investigators, and experiments are in progress in connection with the working up of the tar. The properties of the motor spirit after refining are being investigated in the Ricardo Variable Compression Engine, which forms part of the Station equipment. About 200 tons of the coke have been disposed of to about 180 different purchasers, to each of whom a specially prepared questionnaire was issued. From the replies received it would appear that the coke is very generally found suitable as a fuel for burning either in open grates, kitchen ranges, hot water boilers, or under coppers, but it is not always entirely satisfactory for top heated ovens.

The development of these retorts has been watched with interest by many outside people who have been kept in close touch with the working as it proceeded. The consensus of opinion of those

An idea of the yields may be obtained from the following table :—

Temp. setting.	Coal.	Duration of test. hrs.	Throughput per retort per day tons.	Gas.			Tar in gals. per ton.	Coke.				Remarks.
				Cu. ft. per ton.	Calorific value, B.Th.U	Therms per ton.		Cwts. per ton.	Breeze thro' ½ in. square mesh. %	Volatile matter less moisture.		
										On ¼in. sq.mesh %	Thro' ½ in. sq.mesh %	
620	Nut coal .. Mitchell Main (cold)	96	3·52	4,860	729	35·45	13·1	15·30	11·9	8·4	12·3	Retorts charged at 2-hour intervals; easy working; no trouble.
625	Nut coal .. Mitchell Main (preheated)	96	4·05	4,460	752	33·54	14·31	15·88	11·5	7·3	11·4	Retorts charged at 2-hour intervals; very easy working; no rodding required.
625	Dalton Main. Nuts Through ¼in. 35–43%	74	3·66	5,190	719	37·3	17·3	15·14	17·2	6·6 –	8·2	Retorts charged at 1-hour intervals; very easy working; no rodding required.
625	Garforth Nuts Through ¼in. 18%	72	3·38	6,150	577	35·5	18·4	12·9	19·5	7·7	10·1	Retorts charged at 1-hour intervals; very easy working; no rodding required.

who have inspected the retorts is that they are distinctly promising, and appear to be reaching the end of stage 3 referred to on page 153. Should this conclusion be confirmed by further close tests with freshly mined coal, steps will be taken to have a small commercial setting tried out in some suitable locality in order to investigate thoroughly its economic possibilities, and so to carry the investigations to their final stage, when their success or failure can be judged by actual commercial audit.

It would be inadequate to close this lecture without a reference to the tests of plants developed by outside inventors which have been undertaken by the Division. Some two years ago the Division was authorised by the Government to undertake at public expense tests of any plant which claimed to have reached the end of stage 3. Up to the present time, four plants in this category have been investigated, namely, Parker Plant, Barnsley (Low Temperature Carbonisation, Ltd.); Midland Coal Products, Ltd., Netherfield, Nottingham; "Fusion" retort, Fusion Corporation, Ltd., Middlewich, Cheshire; "Freeman" retort, British Oil and Fuel Conservation, Ltd., Willesden.

Since reports on these tests have been published it is unnecessary to go into detail, but it may be stated that the technical claims made for plants by those responsible for their design have in the main been substantiated. No attempt, however, has been made by the Division to pronounce upon the commercial possibilities of these plants since it is strongly felt that their prospects are so much affected by local conditions that no reliable pronouncement can be made until after they have reached the end of the fourth of the stages enumerated earlier in this lecture.

Time will not permit of dealing with the work of the Division on oil production by methods other than that of carbonisation, beyond remarking that work on hydrogenation in small bombs has proceeded steadily during the past four years, and that investigations in the Bergius Works at Mannheim-Rheinau, are being partially financed by the Department of Scientific and Industrial Research, and supervised by a committee on which there are representatives both of the British Bergius Syndicate and of the Fuel Research Division, in addition to Dr. Bergius himself. An hydrogenation plant of intermediate size (about 1 ton per day throughput), similar in all respects to that at Mannheim, has been installed at the Station. Investigations on the production of motor spirit by synthetic methods are also in hand.

In conclusion, the speaker desires to take the opportunity of extending to the members of the Institution a cordial invitation to visit the Fuel Research Station, and to see for themselves the work which is being carried out there.

DISCUSSION.

The President said he did not think there could be any doubt that it would be the wish of the members that he should convey to the author the thanks of the Institution for his paper, which had been of very great and most unusual interest to them. There were so many authorities present that he would like to hear speak that he proposed to defer until a later stage any remarks that he might desire to make himself for fear that some of their visitors might have to leave before the end.

Dr. W. Cullen said he had been taken by surprise in being called upon to open the discussion. As he told the author before the meeting, he had really attended for the purpose of hearing a little more concerning the last paragraph of the paper. He thought the author had done very wisely indeed in bringing a great many of them back to fundamentals. It was common knowledge to all who had to deal with plant on a large scale that there were four stages through which any process must go before it might be assumed to be a commercial success, and he was very glad the author had emphasized that point. He was afraid that a great many of those present who were interested in oil had been perturbed through reading in the technical press in the last four or five years of the wonderful Press performances of many of the processes for carbonisation at low temperatures. It was possible here and there, where the circumstances were favourable, by the up-grading of slack to achieve, through purely local conditions, commercial success for low temperature carbonisation, where on the one side a comparatively high price was obtained for the coke, and on the other side a comparatively high price for the oil. But he did not think anybody, certainly not the Institution of Petroleum Technologists, nor the corresponding body dealing with fuel economy, had yet arrived at the stage when it was possible to say that any one process, or any combination of processes, would serve the needs of a highly industrialised country like Great Britain.

Dr. R. Lessing said it was very difficult for him to express any opinion on the performances which had been referred to by the author, because he had the privilege of being familiar with the work which was being carried out at the Fuel Research Station at Greenwich. One point that had been referred to by Dr. Cullen must have brought it home to everybody that the object of the work carried out there was, in the first instance, to produce results which could be absolutely relied upon. That, he thought, was the principal function of a Government Department. It was not their function to attempt to invent processes, although, of necessity, in

order to overcome the difficulties that presented themselves it was necessary for them to exercise a very considerable amount of inventive genius. Their principal function, however, was to give absolutely reliable data so that those who were working on commercial propositions, and those who eventually would be responsible for the commercial stage, the author's final stage, No. 4, would be able to do so with success. So very much had been done in the past on the basis of laboratory experiments, or on medium scale experiments, and, as the author pointed out, progress had been greatly impeded by the gambling spirit which had led certain people to go ahead and build plants of commercial size without possessing the data which were absolutely necessary for the successful prosecution of that kind of work. There was one point he desired to call attention to, of which the author was well aware, namely, the necessity of research on the material that had to be dealt with—coal. Until a little more was known about coal itself he thought it was quite impossible for even the greatest genius to devise apparatus for dealing with it. Until a very few years ago very little indeed was known about the subject. During the last few years great progress had been made, and the success which had attended the latest phase of the experiments at Greenwich in the retort shown by the author was really due to the study of coal itself. The pre-treatment of coal, the application of proper methods of heating, of sizing, and of general treatment to any particular kind of coal, had made it possible to obtain results which were, at any rate, on that scale capable of being embodied in a probable balance-sheet. At the recent Conference in Pittsburgh, at which he had the honour of representing the Institution and of attending with the author, they were both able to gather an impression of what was being done on the other side of the Atlantic, and also what was expected from the people on this side. One feature which was strongly insisted upon there, was that, in carbonisation, coal could not be put into a retort anyhow, but that it had to undergo stages in the heating process which altered particularly those characteristics of various coals which produce swelling. The swelling of coal, particularly at low temperature, was the bugbear of the whole process, because it introduced engineering difficulties which they were now only just beginning to overcome.

Mr. F. S. Sinnatt (Assistant Director of Fuel Research) said he desired to add a few particulars to the paper in connection with the kind of tar which had been obtained in the process. The particular point he desired to bring to the notice of the meeting was an investigation which had been carried out on carbonisation of coal at various temperatures in sufficiently large quantities to

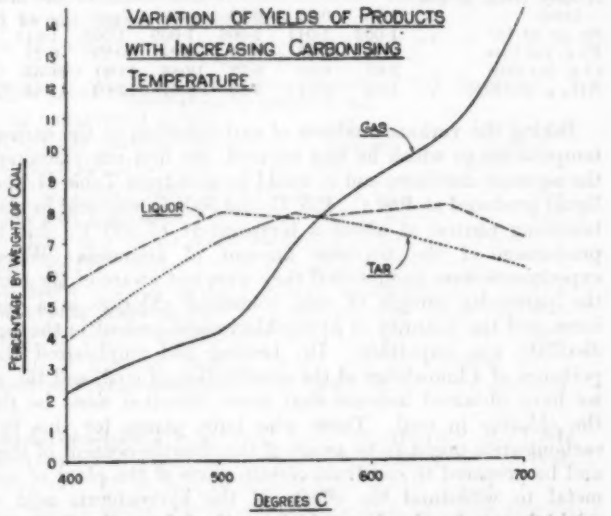
obtain tar to examine fairly exhaustively.* The carbonisation experiments were carried out in the intermediate scale plant which the author has described, working with weights of either 100 lb. or 200 lb., and then repeating the distillation until sufficient tar was obtained for a detailed examination.

TABLE I.

Yields of Products obtained by Carbonisation of a medium Caking Coal at temperatures from 400° to 700°.

Percentage by weight of coal.	Carbonising temperature.						
	400°.	450°.	500°.	550°.	600°.	650°.	700°.
Coke	88·2	83·75	80·50	77·00	75·00	73·00	71·00
Tar	3·9	5·62	7·06	8·00	7·60	6·90	6·24
Aqueous distillate ..	5·6	7·01	7·92	7·70	8·12	8·20	7·18
Gas	2·2	3·32	4·05	7·14	9·10	10·54	14·58
Loss	0·1	0·30	0·47	0·16	0·18	0·36	1·00
Water produced (net)	2·2	3·61	4·52	4·30	4·72	4·80	3·78
Gas, cu. ft. per 100 lb.	34·5	56·2	70·9	126·0	194·3	237·2	356·5
Coke (dry)—							
Volatile matter ..	16·5	13·1	11·6	8·1	5·4	4·5	3·2
Tar (dry)—							
Sp. gr. at 15° ..	0·958	0·980	0·986	1·015	1·039	1·078	1·080
Gals. per ton of coal	9·1	12·8	16·0	17·65	16·4	14·35	12·9

Table I. shows the kind of yields that were obtained at the various



* A study of the tars and oils produced from coal. Sinnatt, King, Linnell. (J.S.C.I., 1926, xlv., 385-393 T).

temperatures. He wished to emphasize the fact that, within the limits of their power, the conditions prevailing during the carbonisation were maintained as constant as possible. The results were given for carbonisation at temperatures varying between 400° C. and 700° C., which were assumed to be the range of temperature covered by the term "low temperature carbonisation," and a fresh quantity of coal was taken for each separate temperature. He desired to draw attention to the yield of tar, which was 8 per cent. of the coal, at a temperature of 550° C.

When the values were plotted in the form of a graph, it became evident that at about 550° C. there were changes of considerable interest. The aqueous distillate reached its maximum in the experiments at 500° C., but somewhere in the neighbourhood of 550° C. there was a critical point. The gas evolution was most rapid above that temperature, and at 600° C. it had become quite marked.

TABLE II.

Composition of Liquors.

Carbonising temp. ..	400°	450°	500°	550°	600°	650°	700°
Reaction	acid	acid	acid	neut.	alk.	alk.	alk.
Colour	pale yellow	pale yellow	purple	yellow	reddish	nil	reddish
Acidity (HCl, g. per litre)	1·05	0·57	0·09	—	—	—	—
Sp. gr. at 15° ..	1·003	1·011	1·006	1·009	1·009	1·015	1·016
Fe g. per litre ..	0·44	0·55	0·37	0·24	0·28	0·21	0·15
Cl g. per litre ..	2·61	6·80	9·72	12·86	18·41	14·35	15·24
NH_3 g. per litre ..	1·24	2·27	3·23	6·61	12·06	11·64	15·68

Taking the various products of carbonisation at the carbonising temperature to which he had referred, the first one examined was the aqueous distillate, and it would be seen from Table II. that the liquid produced at 400° C., 450° C. and 500° C. was acid in reaction, becoming neutral at about a temperature of 550° C., due to the production of the requisite amount of ammonia. When the experiments were commenced they were not aware of the fact that the particular sample of coal contained chlorine in a peculiar form, and the quantity of hydrochloric acid present in the aqueous distillate was important. Dr. Lessing had emphasized the importance of a knowledge of the constitution of coal, and the results we have obtained indicate that more attention must be paid to the chlorine in coal. Those who built plants for this type of carbonisation ought to be aware of the chlorine content of the coal, and be prepared to construct certain parts of the plant of suitable metal to withstand the effects of the hydrochloric acid which might be produced. It would be noticed from the figures in the table that the aqueous had dissolved a part of the plant, as the

amount of iron present in the liquid obtained at the lower temperatures is considerably greater than at the higher temperatures:—

TABLE III.

Constitution of Tar Oils 400° to 700°.

Percentages by weight of oil.

	Temperature of carbonisation, °C.						
	400°.	450°.	500°.	550°.	600°.	650°.	700°.
Phenols	24·55	29·12	29·20	29·31	32·97	35·45	35·98
Bases	1·62	2·06	2·35	2·66	3·00	3·15	2·54
Neutral oil	73·80	66·98	66·05	67·77	62·87	60·11	60·03
Unsaturated compounds	44·0	46·1	45·4	47·3	48·4	50·9	52·2
Saturated oils ..	29·8	20·9	22·9	18·5	13·4	8·6	6·2

Passing on to an examination of the tars, he desired to draw attention to the different proportions of constituents present. In the case of the unsaturated compounds and the saturated compounds of the tars, it would be noticed in Table III. that the saturated compounds decreased rapidly above 650° C., the low percentage of 8·9 being obtained, whereas in the types of tar at a lower temperature there was a very considerable proportion of saturated compounds. The phenols were relatively high. They were reasonably constant between 450° and 550°, but they gradually increased at the higher temperatures.

TABLE IV.

Comparison of Distillation and Solution Methods of Tar Treatment.

Percentages by weight of tar.

	Solution method.		Distillation method.	
Phenols	26·1		23·3	
Phenol		0·3		0·3
Soluble in light petroleum		19·6		19·7
Insoluble in light petroleum		6·5		3·5
Bases	2·7		2·5	
Unsaturated compounds	6·6		8·1	
Refined oils	41·6		33·5	
Volatile to 360°		33·3		31·4
Insoluble in methyl sulphate		19·4		15·5
After treatment with conc. sulphuric acid		8·2		7·0
Solid paraffin, m.p. 62°		0·1		0·1
Pitch			32·3	
Precipitate from light petroleum ..	13·9			
Ether	0·9			
Dilute acid	8·1			
From distillation of refined oil		8·2		2·1
Total pitch		(31·1)		(34·4)
	99·9		99·7	

Table IV. gave a comparison of the distillation of one of the low temperature tars and separation by means of solvents. Much

work had been, and was being, done upon the separation of tars by means of solvents. They had examined one of the tars from the large scale low temperature carbonisation plant the author had described, and the particular point to which he wished to draw attention was that the pitch obtained by distillation of the tar was about 32 per cent., and from the refined oil an additional 2 per cent. of pitch was obtained above about 340° C. In the separation by means of solvents a pitch-like precipitate was continually being obtained. They obtained a precipitate when the tar was treated with light petroleum, later when treated with ether, and when the unsaturated compounds were treated with dilute acid. When the refined oil was distilled a small proportion of pitch was obtained, and all those added together came, strangely enough, to about 31 per cent. It thus appeared that, by treating with solvents, the total amount of pitch obtained was not much different from that obtained by ordinary distillation. Therefore the method of distillation would appear not to be so destructive as was generally assumed.

Dr. W. R. Ormandy thought that in so far as the author dealt with matters of fact, it was difficult to say anything about the paper. It was astonishing to find a Government desiring to give the investor in low temperature distillation an opportunity of protection. Naturally we could only conclude that this sensible action of the Government arose from the fact that the Department of Scientific and Industrial Research was controlled by technical and scientific people. At any rate, the fact remains that a Government was willing to test, free of cost, any low temperature process which had reached a stage which entitled it to appeal to the public for funds.

With reference to the Bergius process he thought the Government was to be congratulated upon having had the foresight and the wisdom to step in at an early stage and put themselves in a position to obtain full access to all the knowledge that was obtainable in Germany with regard to the subject. It was interesting to know that the Fuel Research Division had been able to distinguish between certain very uncommon coals which did not readily react under hydrogenation conditions and others which did, though both classes of coals reacted similarly to the bulk of the tests which might be applied. This bore out the points which have been so ably raised by Dr. Lessing.

He thought the paper was admirable, and that it would tend to disprove or to overrule a very large amount of baseless and useless criticism which had been made about the Fuel Research Division of the Department of Scientific and Industrial Research. There had been a lot of what he might call biased criticism, and he thought

it was only by means of papers such as Dr. Lander's that it was possible to judge the value of the work that has been done. There was only one other remark he desired to make with regard to the Fuel Research Division. They might be, and were, he thought, extraordinarily efficient in the work they did, but they could certainly do with a better advertising agent. Not only the Fuel Research Division, but many Government Departments, possessed amounts of extraordinarily valuable information, but the world at large did not know that the information was there, or, if they knew it was there, they did not know exactly where to go for it. If there were a Publicity Department in connection with Government Departments, supplying information for the benefit of the community as able as those which existed in America, it would be a very great benefit to the industry at large.

Prof. J. S. S. Brame said he was sure the Members of the Institution were deeply indebted to the author for the invitation he extended to them at the conclusion of his address to visit the Fuel Research Station at Greenwich, and he thought the Council of the Institution should consider this invitation and arrange a convenient date for such a visit. The published reports of the Fuel Research Board were reviewed in the Journal of the Institution, and other Journals, but he did not think enough weight was attached to the work which was being done, and certainly much of the criticism levelled at the Research Board was unjustified. There were one or two points in the paper upon which he desired the author to throw a little more light. The Members of the Institution thought they knew what oil was. He therefore desired to ask the author what tar was. The title of the paper was "The Production of Oil from Bituminous Coal," but Mr. Sinnatt had shown on the screen a slide giving the composition of low temperature tar showing 35 per cent. or thereabouts of pitch. He would like to ask: When did tar become oil? That was, he thought, a very important point, because he was afraid the word "oil" had been used too much when something else was correct. Some of the members were interested in the possibility of the processes described from a commercial point of view, and another point upon which a little further light might be thrown was in connection with the statement that, "with the high prices for oil which were ruling at about that time it was almost possible to see a balance between working costs and returns." It was subsequently stated that at that time the price of oil was over £15 a ton, at which price he gathered that the process very nearly paid. As it was further stated that the price of oil soon fell to about £3 a ton, he desired to ask at what stage the process would have paid. One way in which he thought the work of the Fuel

Research Board would benefit the country very greatly was that it would be a revelation of the scientific possibilities of British coals as distinct from their fanciful possibilities. In that way the expenditure of enormous sums of money, probably of public money, would be prevented. Many people at the present time were looking upon "oil" from coal as promising the salvation of the coal industry. A prominent politician, in a speech recently delivered, stated that "it would probably be possible to produce from coal a fuel at a price which would displace oil, and if that were done, then technically the great mining industry would be saved." The work of the Fuel Research Board might lead to public money not being wasted in the erection of enormous plants with the object of proving that oil could be made better in this country than it could be bought. At the present moment it seemed to him that things were running riot in that way. If the reports of the Fuel Research Board could only penetrate into such quarters they might do a vast amount of good.

Mr. E. H. Cunningham Craig desired to associate himself with the remarks Dr. Ormandy had made in regard to the various criticisms that had been levelled against the Fuel Research Station. He had never visited that Station, but he had often heard people ask what had been done for all the money that had been spent upon it. The author had demonstrated most clearly in his paper that the Station had produced a great amount of exact data upon a number of very important and interesting points. He agreed specially with what the author had said about local conditions, because it was essential to consider the prices at which the various products could be sold locally. The author had referred to the Cannel Coal Committee of the Institution. As one of the originators, and one of the technical advisers of the Cannel Coal Committee, he desired to explain that the Fuel Research Station had by no means trespassed upon any of the ground that that Committee tried to cover at that time. The Cannel Coal Committee was not interested in ordinary normal coal nor in tars, their object being to make the best kind of oil possible, oil which did not give a precipitate when mixed with petroleum. The research, so far as it went, very soon showed that it would be necessary for the Committee to confine themselves for those purposes to cannels and canneloid material. A great deal of research work was done, and it had been continued in various ways since. Although, as the author pointed out, no process had perhaps reached the fourth stage, he could assure him that very soon one or two processes would have done so. He hoped figures would be produced, perhaps not exact as those the author had given, but figures that would show how a profit could be made; but he was afraid that would

not take place yet from normal coals. He desired to ask the author, in conclusion, whether he felt at liberty to state at what price he was able to sell the semi-coke.

Mr. E. R. Redgrove desired to ask the author or Mr. Sinnatt if, from their investigations, they thought there was any possibility of obtaining lubricating oil from coal oils. He believed it was publicly stated in the Press a few days ago that this country might be able to obtain all the oil products it needed from its coal. He thought it quite possible that that was true in so far as spirit and fuel oil were concerned, but he had grave doubts about lubricants. During the war he had occasion to examine several samples of lubricating material taken from captured German rolling stock, aeroplanes and such-like machinery, and towards the latter part of the war the samples analysed left little doubt but that they were obtained from coal, possibly a soft cannel coal, or even peat. It was said that the Allies went to victory on waves of oil, and that Germany lost the war because of the lack of oil. If the Germans were brought to such a state for lubricants as they appeared to be by the samples which he analysed, he could quite believe that no machinery would run for any length of time on such products. Dr. Ormandy had said that if this country were involved in another war, it might be necessary for it to obtain all its petrol from sources which existed in this country. Personally he would say that that applied not only to petrol but also to lubricants, because machinery could not be run without efficient lubrication. If there was any hope that lubricants might be produced from coal oil, he thought the information would be welcome to the members of the Institution.

Mr. E. A. Evans thought it would be of interest if he stated, in regard to the remarks made by Mr. Redgrove, that he believed the only lubricating oils that had been produced with any claims of success were by Mr. Maclaurin, to whom reference was made in the paper. He would like to ask the author whether he had any information with regard to those oils.

The President, in closing the discussion, said there was one remark he desired to make which might save the author a certain amount of time in replying to the discussion so far as it related to criticisms levelled at the Fuel Research Board. The whole of that criticism could be summed up in one expression, namely, that it was due to the fact that any Research Station of the sort did its most important work generally when its results were negative. It was the negative results that were of a kind that could not be produced by any private Institution. It was those results which did not appear outside, and so gave the impression to the public that value was not being received for the money spent

on the Fuel Research Station. After all, what had been spent on it? From its beginning up to the present time it represented about the price of one submarine. He thought the Admiralty were quite capable of experimenting on bigger units than that. The money had been spent in connection with work that might be, not only of very great financial importance to the country, but of serious importance from the point of view of military security. Those who remembered in the early days of Coalite, and the companies that split off from Coalite, Limited, and who remembered the amount of money that was handled without justification by experimental work, would realise how important from the public point of view the Fuel Research Station was as an institution to which they could go with confidence and get negative as well as positive results regarding the technical efficiency of the various processes that were suggested as commercial schemes.

Dr. C. H. Lander, in reply, said that Dr. Cullen had asked for a little more information about the Bergius process. All he could say was that, in regard to the intermediate scale of the process, from being a doubting Thomas, and from having a certain modicum of philosophic doubt, he had become absolutely convinced that the technical problem was proved that there could be produced from coal something like 50 to 60 per cent. of a liquid product, a distillable oil; from 15 to 20 per cent. of gas; from 10 to 15 per cent. of solid organic matter; 10 per cent. of ash and moisture. Those figures did not total up exactly to 100, but they were broadly correct for the purpose; and the process had been worked on the ton a day scale. Larger units were going to be used, and so far as actually doing the work was concerned, there were not, in his opinion, likely to be any very striking difficulties to be overcome in going up to those larger units. Of course, the important question was: "Would it pay?" And that was not yet known.

He thanked Dr. Lessing for his remarks, and particularly for pointing out that it was not the function of the Station to invent processes but to obtain data. That was one of the points that he had endeavoured to impress upon the members in the course of his paper. The Station was not striving to invent processes. In the developments described it had simply tried to do a certain job in an existing process.

He also desired to thank Dr. Ormandy for his kind remarks. He agreed that information as to the activities of the Fuel Research Station was not so widespread as was desirable, but it was somewhat difficult to know how to remedy such a state of affairs. There was always to a certain extent a bottle neck, composed of himself and one or two of his senior assistants, past which everything had

to get in a right and proper form. One very important matter that had been referred to was that in the running of the Station a large mass of data that could not possibly be put down on paper was accumulated from day to day, and for that reason those in charge welcomed at the Station people who were genuinely interested in the subjects dealt with in order that they might see for themselves what was being done. The Fuel Research Station Staff received a great deal of information in this way; in fact, they were being educated every day; and not infrequently visitors saw something at the Station which had not occurred to them before, and on talking the subject over with the particular individual who had been working on the point, benefit frequently resulted.

Prof. Brame had asked him a question with regard to the definition of tar. He found that in a report of the Station on the Freeman Retort the following statement appeared: "The term 'tar' is applied to the crude liquid product of carbonisation other than water. It is from the 'tar' that the various grades of 'oil' are obtained." That was how those of the Fuel Research Station looked at it. The use of the term "oil" for crude tar had only had one origin, namely, the individual financially interested in making it appear that a messy material which contained 30 per cent. of water and 50 per cent. of pitch was an oil. He was unable to answer the other question that Prof. Brame had asked him, namely, at what level of oil prices the process would have paid? He could not say. At the time in question the country was suffering from the aftermath of the war. As members of the Institution would recognise, the Station had always to prepare two balance-sheets for any work that it carried out, the first being the normal industrial every-day sort of balance-sheet, and the other one an emergency balance-sheet in which prices that were not commercial were taken, the prices which had to be paid during a time of national emergency. He quite agreed with what Mr. Cunningham Craig had said. He thought the two or three installations which were now being erected for the utilisation of cannel were likely to prove sound propositions, and that they would certainly pay long before there would be any payment of dividends from the low temperature carbonisation of bituminous coal.

He hoped the President would allow Mr. Sinnatt to reply to the question that had been asked in regard to lubricants.

Mr. F. S. Sinnatt, in reply to Mr. Redgrove's question in regard to lubricants, said the Fuel Research Station had been concerned with that question, and he thought the best reply he could give was to say that as far as their tars and oils were concerned, they had not found a fraction which would satisfy them as a lubricant. It was perhaps, however, not out of the range of vision that some

of the oils at one of the temperatures which he had described that evening might prove to contain a fraction which would be suitable for lubricants. They appreciated the fact, however, that statements had been made that certain tars from low temperature carbonisation contained a fraction which could be used as lubricants, but they thought the tests that had been applied had been insufficient; they had not been put through the rigid test of actual usage.

He thought that it should be made perfectly clear that although certain tars might contain fractions which could be used as crude oils for the production of lubricants, emphasis should be placed on the necessity for careful refining, and this would raise their price to that prevailing for lubricating oil produced from natural petroleum.

Dr. Lander, continuing his reply, said he desired to express his thanks to the various speakers in the course of the discussion with regard to the criticisms that were levelled at the Fuel Research Station.

Such criticism usually came from sources which could safely be disregarded, but at the same time the Department welcomed constructive criticism, which was of great value.

The meeting then terminated.

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDREDTH GENERAL MEETING of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, Adelphi, W.C., on Tuesday, March 8, 1927, Sir Thomas Holland, K.C.S.I., K.C.I.E., D.Sc., F.R.S. (President), in the Chair.

The President said the members would be interested to know that that meeting was the hundredth General Meeting of the Institution. The inaugural meeting was held in the room in which the present meeting was taking place on March 3, 1914, and meetings had been held regularly ever since—even during the war.

There was one further announcement he desired to make—namely, that the Annual Meeting, followed by a General Meeting of the Institution, would be held at the Royal Society of Arts on Tuesday, March 22. At the General Meeting three or four papers would be read, on which the Council would afterwards consider the question of formulating propositions for the Empire Congress of Mining and Metallurgy to be held in Montreal next August. As the papers to be read at the meeting would be submitted afterwards to the Congress, it would be improper if the Institution allowed those papers to be published in advance, so that possibly the Council would decide that the papers read on the 22nd inst. would not be available for the press. The discussion on the papers would be taken into consideration in formulating proposals for the Congress, and in consequence would be treated as confidential also. The subject had not yet been formally before the Council, but he knew there was a general feeling that the papers ought to be kept in reserve until they were actually read before the Congress, and then they would become available in the Journal in the ordinary way.

The following paper was then read :—

" Two Shallow Oilfields in Texas—A Detailed Study."

By ARTHUR WADE, D.Sc., A.R.C.Sc., F.G.S., M.Inst.M.M., F.Am.G.S. (Member).

I.—INTRODUCTION.

The fact that the United States of America produces more than three times as much oil as does the rest of the world gives rise to peculiar conditions which are sometimes not appreciated by outsiders.

The great variety of conditions under which petroleum occurs, the widely distributed oilfield areas in one limited geographical region, the vast number of operators and operating concerns, the proximity of large centres of population with factories, workshops, supply houses and markets produce conditions of strenuous competition in forms which exist nowhere else. One result of this is that new methods are tried and old methods abandoned with greater readiness than elsewhere so that change and evolution are rapid in every branch of the oil business. Again, in consequence of some of the factors mentioned above greater opportunities arise for the small company and the individual operator than in most oilfield areas. Land for drilling purposes can frequently be obtained on very easy terms, and for the expenditure of a few hundred dollars a well can be drilled, especially where oil sands exist at shallow depths. Very many shallow fields have been opened up in this manner, especially in the States of the Middle West and South, and many sands which have returned good profits on comparatively small capital expenditure have been developed at depths varying between 150 feet and 2000 feet. The larger companies have in the past shown a tendency to ignore these shallow horizons, and cases are known where drillers have been reprimanded for taking time to test and report them. The sequel in one such case was interesting. The driller waited for about twelve years, until the company had abandoned its wells from a deeper sand. Then in company with the local barber, baker and teamster, he acquired a portion of the area, put down a well which yielded 100 barrels of oil a day from a depth of about 500 feet and greatly improved the financial condition of the enterprising members of the little syndicate.

The independent oilfield geologist and technologist finds such conditions very favourable to his existence. Though there has been a tendency, which still exists, on the part of the small operators and companies to despise the work of the geologist and expert, a tendency which is due in part to the poor quality of some of them and to the fact that it has been easy for the charlatan to enter this field of work, the spread of knowledge and the successes won largely by the geologists of the major producing companies in discovering and opening up new fields is rapidly dispelling such an attitude of mind. Moreover, a great trade has developed in the sale and exchange of small producing leases both fully and partly developed, undeveloped acreage near to producing wells and "wildcat" leases in more speculative areas. There are, in many centres, brokerage establishments which do no other form of business. The independent geologist has become an important factor in such transactions. Not only is he called upon to furnish reports on the structural conditions and prospects of such areas, but he has frequently to examine the

present condition and productivity of the oil and gas wells which may be present, to inquire into their history, forecast their future, discover possible presence of water, estimate the possible future encroachment of water, lay down a programme for future development, set forth the number of wells that may still be drilled on the property and the production of oil that may be obtained therefrom, calculate the effects of offset drilling on neighbouring properties, in short, examine and report upon all factors upon which a scientific valuation may be founded and usually to suggest the actual present value of such properties to his clients.

Finally, the exigencies of the Federal Income Tax Commissioners have created a situation which frequently leads to calls upon the services of the consulting geologist. It is obvious that the income derived from the production and sale of oil on most small properties may be represented by a downward curve, which must touch zero in a few years time, that is, production will decrease until it is unprofitable to continue work upon the wells and the property is abandoned. The producer is therefore allowed to amortise his income tax on the basis of the probable life of his wells and his diminishing returns. For this purpose it is necessary to call in an independent expert to make an examination and prepare the necessary details for the Income Tax Commissioners, and in most cases the results are accepted by them. Such work does not frequently fall in the way of British petroleum geologists and it may be useful to set forth in this paper the methods used and results obtained in the study of shallow oilfields operated entirely by small companies and individual producers for the purposes mentioned above. With this in mind, two of the shallow oilfield areas of which the author has personal knowledge, have been selected dealing with one in some detail, and more briefly with the second, which has been introduced mainly for purposes of comparison.

II.—The Sipe Springs Field.

A. *Geology.*—The Sipe Springs shallow oilfield is situated near the northern boundary of Comanche County in North-Central Texas. The area is an inlier occupied by members of the Canyon Group of the Pennsylvanian Formation entirely surrounded by Cretaceous deposits, which spread across the belt of Pennsylvanian strata in this part of Texas, overlapping each group in turn from East to West and dividing the outcropping Pennsylvanian of Central Texas into two parts. This unconformable Cretaceous cover is obviously very thin in this area, and the different members of the Pennsylvanian succession can be traced across the break caused by its presence without difficulty (Fig. 1).

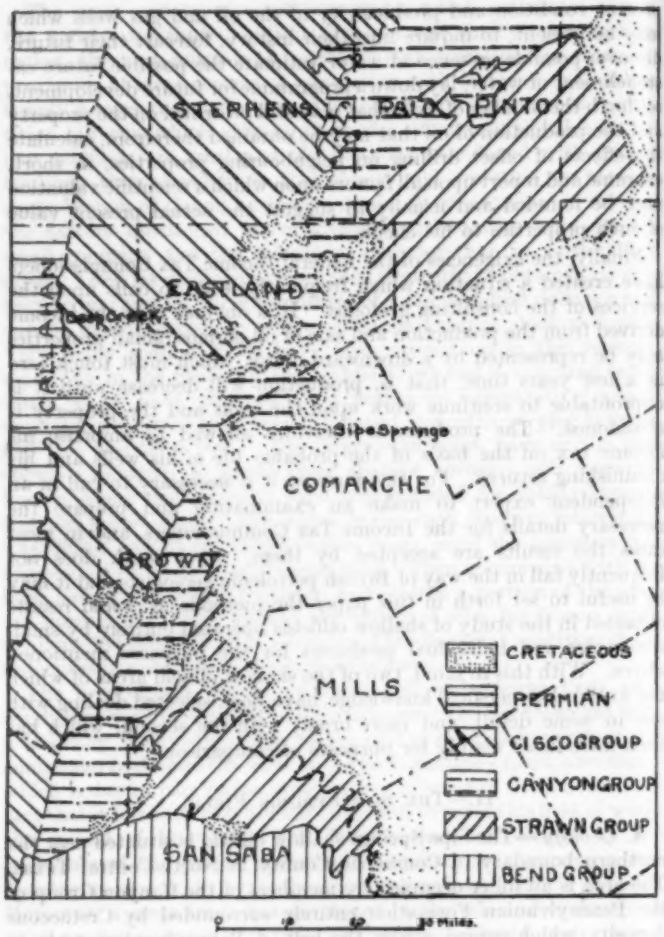


FIG. 1.

GEOLOGICAL MAP OF PART OF NORTH CENTRAL TEXAS BASED ON MAPS BY PLUMMER AND MOORE.

The country consists of gently rolling plain intersected by small and inconsiderable water courses with sharp ridges of the Ranger Limestone to the West. The beds underlying the plain consist of

blue and grey marls containing lenses of sand and thin limestones belonging to the Canyon Group of the Pennsylvanian. The beds dip to the West almost imperceptibly, in fact, little evidence of dip is obtainable excepting in the overlying limestones and then it must be obtained by levelling over a considerable area. There is, however, a more or less well defined terracing of the plain running from North to South, with a fall away to the East, a very poorly defined escarpment due to the presence of thin bands of limestone in the marls, but of these there is no definite exposure at the surface.

The presence of oil at shallow depths was suspected owing to the discovery of small quantities in water wells put down by neighbouring farmers and a site for a "wildcat" well was chosen for an independent operator a little way back from the edge of the ill-defined terrace in the marls. Small but profitable production of from 20 to 30 barrels of oil per day was obtained from a depth of a little over 200 feet. The cost of drilling the well was little more than $400·00. Others entered the field and eventually upwards of 200 productive shallow wells were drilled on this area together with a number which proved unproductive.

In order to indicate the nature of the Canyon strata passed through in drilling, sections of three wells selected to show the dip of the producing horizon are given in Fig. 1A.

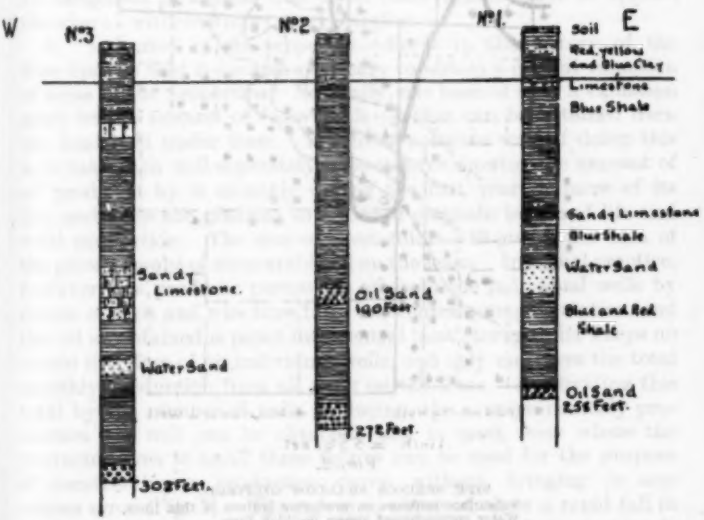


FIG. 1A.

TYPICAL WELL SECTION ACROSS THE SIPE SPRINGS SHALLOW OILFIELD, SHOWING DIP AND VARIABILITY OF CANYON STRATA.

It will be noted that two oil sands are present, one at from 180 to 200 feet below the surface, and the other from about 260 to 300 feet. The upper sand is rather erratic and lenticular, and only yields oil in places, though several wells obtained profitable supplies from this horizon. The lower sand is more persistent and productive throughout the field.

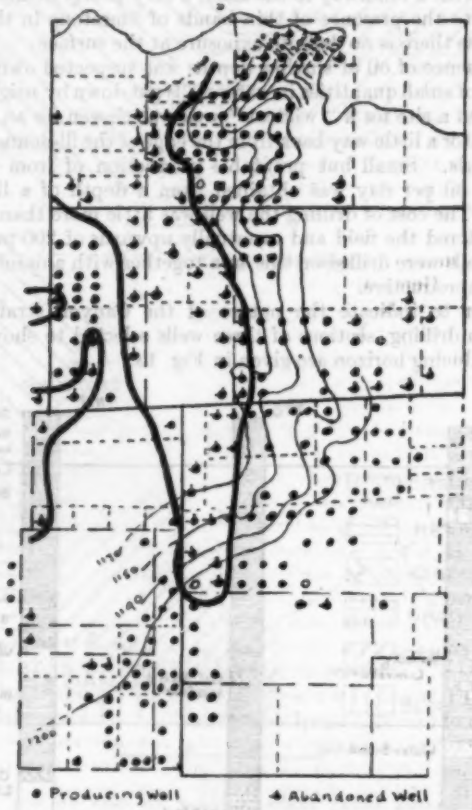


FIG. 2.

SIPE SPRINGS SHALLOW OILFIELD.
Subsurface contours on producing horizon in thin lines. Water encroachment shown in thick lines. Contours given in heights above sea level.

As drilling operations extended it became possible to construct a structural map indicating the configuration of the surface of the producing sand by means of sub-surface contours (Fig. 2). The results show that there is a general dip of the beds to the west, at about one in thirty, the strike being almost due north and south, though in the southern part of the area it changes to north-east—south-west. The plane of dip is affected by small puckers, the axes of which may run either north-east—south-west or north-west—south-east. The best producing wells are those situated on or near to these minor folds. Although the general directions of dip and strike and a rough idea of the structure were obtained in the preliminary geological examination of the area, and provided sufficient data upon which early wells could be located successfully, there was very little evidence of the minor folding that could be observed at the surface. By comparing the sub-surface structural map with the surface features some relationship could be established which was useful in later work in that it showed that small variations in level could be connected with important structural conditions. Generally speaking the more productive areas have been those situated on low-surface rises which again showed a connection between topographical feature and geological structure. Although this proved to be the case in this field it would, of course, be dangerous to assume that these observations could be applied elsewhere, without very great caution.

B. *Valuation of the properties.*—Early in the history of the Sipe Springs field it became necessary to obtain a careful valuation of some of the properties. Naturally, the basis of such a valuation must be the amount of recoverable oil that can be obtained from the land held under lease. The most accurate way of doing this is to take each well separately, plot a curve showing the amount of oil produced by it monthly during the first year or more of its life, and from the gradient so obtained estimate length of life and total production. The sum of these totals will give a fair idea of the gross amount of recoverable oil on the lease. In actual practice, however, the producer pumps his oil from the individual wells by means of rods and wire lines from one central pumping station, and the oil so obtained is piped into central tank storage. He keeps no record therefore of his individual wells, and only measures the total monthly production from all wells on the lease. By dividing this total by the number of wells producing, the average monthly production per well can be obtained, and in most cases where the producing area is small these figures can be used for the purpose of constructing a production curve without bringing in any serious error (Fig. 3). The curves so obtained show a rapid fall in production during the first six months, after which production is

represented by a straight line which is falling very gradually towards zero point. From the nature of this line, together with a consideration of geological factors, the life of the well can be estimated as well as the quantity of oil likely to be recovered. In most cases a life of approximately ten years was estimated for the wells. Curves obtained from wells drilled on leases which were

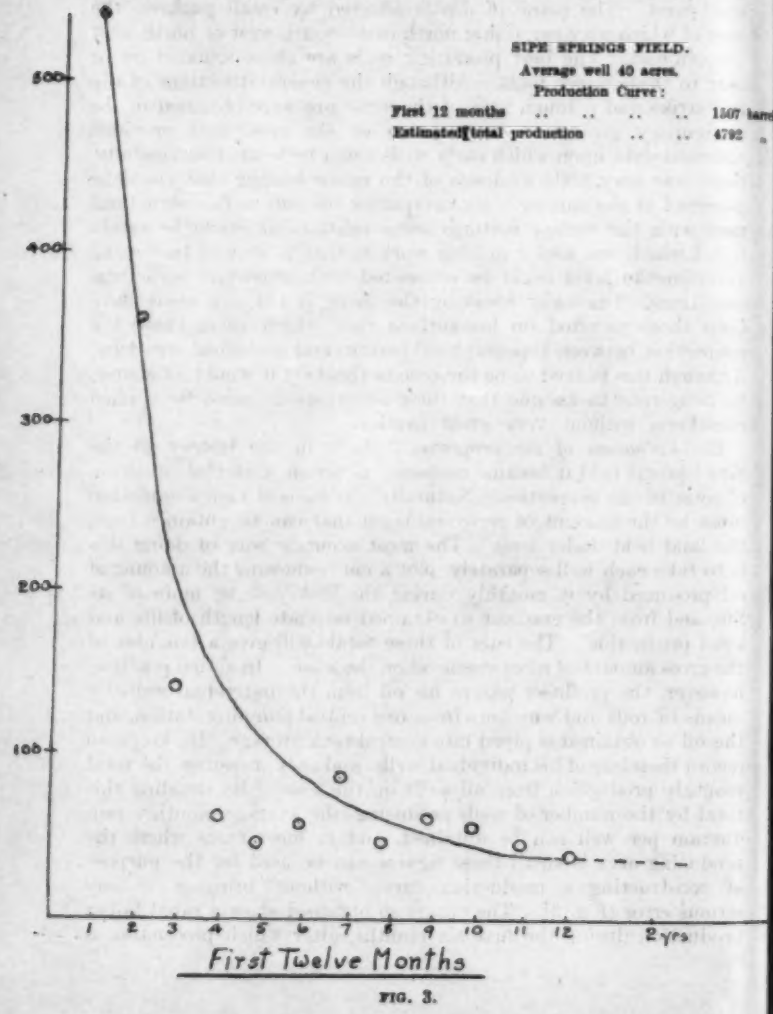


FIG. 3.

less fortunately situated on the zone of production distinctly showed that a shorter period of productivity was to be expected, and lives of from five to six years were estimated. Most of the wells started production at from 20 to 50 barrels of oil per day, but at the end of the first year this production had settled down pretty uniformly to two barrels a day, which, as subsequent investigation showed, was held for two or three years, a slight temporary increase being obtained after wells had been cleaned out.

To estimate the total value of these properties the number of productive wells that could be drilled with economic spacing was taken into account, and it was assumed that these wells would be drilled by the producers. By this means the gross value of the property in terms of recoverable oil was obtained. From this, however, must be subtracted the amount of oil represented by royalties provided for in the terms of the leases. As a rule the lessee contracts to give the lessor a royalty amounting to one-eighth of the gross production. The value of the remaining oil is calculated from the price being paid by the pipeline companies at the time of valuation. Further deductions have to be made for the expenses incurred both in fully drilling the areas held under lease and those incurred in the general work on the lease such as pumping, cleaning and conveying to storage and pipelines. For example, in one case the average cost of drilling the wells worked out at about $1400·00 per well. Operating costs averaged $775·00 per month. In eight months 15,413·65 barrels of oil were raised. Deducting one-eighth for royalty we get 13,487 barrels of oil. The cost of pumping, storing, conveying to pipeline, etc. was $6200·00, thus the operating costs worked out at 46 cents. for each barrel of oil put into storage. The oil is of good quality, having a specific gravity of 0·83 or between 38 and 39 on the Baumescale. The price paid by the pipeline company at the time was $2·75 per barrel, the pipeline company connecting its own line at its own expense, with the storage tanks on the lease in order to take delivery.

Details of a typical valuation are given below :—

TABLE A.

Producing horizon 270 feet in depth.			
Gravity of oil from discovery well 38–39 Baume.			
Initial production of discovery well 40 barrels a day.			barrels.
Ultimate production (estimated) of average well			4,792
Total recoverable oil (estimated) from 12 wells to be drilled ..			57,504
Less one-eighth royalty			7,188
Net recoverable oil			50,316
Value of net recoverable oil at $2·75 per barrel		$138,369·00	
Less cost of 12 wells at $1365·00 each (*See Table* B.)	$163,80·00		
Less cost of producing 50,316 barrels at 46 cents per barrel (*See Table* C.)	$23,145·00		
	$39,525·00		
Net value of lease		$98,844·00	

TABLE B.

DRILLING COSTS.

Itemized Cost of One Well.

	$	$
Drilling (contract) at $3·00 a foot, average depth 270 feet	810·00	
Two days day-work at $35·00 a day	70·00	
		880·00
Slush pit		30·00
250 feet casing at $1·40 per foot		350·00
Casing shoe		27·50
Two-way common casing-head		6·50
270 feet 2-inch tubing		81·00
6 feet 10 inches steel working barrel and valves		10·00
270 feet sucker rods at 10 cents. a foot		27·00
6 feet 10 inches by 1½ inches polish rod		5·00
Miscellaneous 2-inch connections		25·00
L.G. and J. steel pump jack		40·00
Clevises, hooks and throw-off hook		10·00
Total		1492·00

NOTE.—Prices include cost of delivery on lease.

A good idea of the average cost of drilling a well on the leases may be obtained from the following:—

No.	Drilling. $	Equipment, etc. $	Total. $
1	890·00	274·28	1164·28
2	972·25	508·36	1480·61
3	887·25	577·53	1464·78
4	834·00	416·84	1250·84
5	843·00	577·56	1420·56
6	801·00	585·76	1387·66
7	770·25	602·16	1372·41
8	813·00	564·12	1377·12

Average cost per well $1364·79.

TABLE C.

Monthly Cost of Lifting.

	$
Two pumpers	360·00
One roustabout	165·00
Fuel	150·00
Miscellaneous expenses	100·00
Total	775·00

First Year's Oil Runs from Three Small Leases.

Month	40 Acres.	28 Acres.	5 Acres.	
January	1072·56	—	—	barrels
February	2470·98	—	—	,,
March	398·12	1539·98	335·26	,,
April	190·44	1732·88	168·00	,,
May	146·92	1462·58	141·00	,,
June	175·44	1292·29	255·88	,,
July	251·62	1932·72	126·88	,,
August	123·93	1531·17	65·00	,,
September ..	173·57	1407·43	66·04	,,
October	158·19	1178·18	71·76	,,
November ..	129·56	1017·30	73·32	,,
December ..	112·04	1008·07	71·76	,,
January	125·18	955·60	75·92	,,

C. *Encroachment of Water.*—About three years later I found that though most of the older and better situated wells were standing up well to the estimated production, salt water was encroaching from the north-west and was affecting the more recently developed western portion of the field. The line of approach was along a synclinal depression running north-west to south-east, well shown on the structural map. The area of the sand so flooded is shown on the accompanying map (Fig. 2). Water had also made its appearance in the sand in a tract isolated from the main body of waterlogged sand and to the west of it. This is probably a local area of depression which has some channel connecting it with the main body of water though this channel may be quite narrow. The water was found to be encroaching upon the oil-bearing area at the rate of about 50 acres per annum.

A feature of the Sipe Springs field is the comparative absence of gas in the oil horizons so that pressures are low. It is evident therefore that the flow of the oil in the wells is largely due to hydrostatic pressure. The presence of the water and its movement up the dip of the beds is therefore probably very advantageous to the wells which are high on structure and must be regarded as a favourable factor so far as ultimate production is concerned.

The later drilling demonstrated that productive areas existed in the sand further down the dip. A terrace was located some distance to the west, where the sand was about 400 feet below the surface and good production was being obtained. The field was extending also both to north and south.

III.—The Deep Creek Oil Field.

The second shallow oilfield to be briefly dealt with is situated on Deep Creek, a small stream running through the northern part of Callahan County, Texas, about eight miles north of the small

village of Putnam on the Texas and Pacific Railway. The country consists of somewhat desolate red soil plains stocked rather sparsely with cattle. Low "mesas" occur here and there where patches of limestone have resisted denudation and are all that remain of a former covering. Deep Creek cuts a winding, vertical walled trench through the area, but has made no decided valley. The strata forming the surface belonged to the Putnam Formation, a group of strata of uncertain age which lies between the uppermost or Cisco Group of the Pennsylvanian and beds which definitely belong to the Permian. Red, yellow, green and grey clays and shales predominate with well-established limestone horizons, both above and beneath. A few lenticular sandstones occur in the clays, and in these salt water, gas and petroleum are to be found (Fig. 4).

So far as geological structure is concerned little guidance is obtainable from a surface examination. Outcrops are wanting in the clayey plains. In the ravines the shales provide only muddy banks, while the occasional bands of limestone are broken and erratic and, being nearly horizontal, small local irregularities obscure the real nature of the dip. It is possible, however, to obtain information by tracing levels on some recognisable limestone horizon in the "mesas." A low general dip to the west was established though dips of greater amount were observed locally. In the "mesas" the underlying shales weather away rapidly, so that great blocks of limestone up to 20 square yards in extent have been undermined and have been displaced on the sides of some of the hills, the displacement sometimes being so small and overgrown that unwary geologists have taken the angle of slope of the fallen blocks as being the true dip of the strata. The geologists of one of the larger oil companies allowed themselves to be so deceived in one such case, and in consequence a costly hole was drilled to a depth of over 4000 feet without success. The drilling of this dry hole, however, was the cause of subsequent development by small operators since the logs showed that several showings of oil were passed through at shallow depths. The first shallow bore was, through equally faulty geological observation, located on the summit of one of the "mesas" and was also dry. On my advice a second well was drilled on the plain to the east and oil was struck at a depth of about 395 feet. Subsequently it was found that a second productive sand existed at a depth of about 470 feet. The sands were very erratic and lenticular thickening, thinning, disappearing altogether and occasionally passing into limestones between wells which were drilled at intervals of 300 feet. The 395 feet sand was particularly erratic, and was only occasionally productive of oil. In other wells it yielded gas or salt water, or was altogether absent. The deeper sand was more persistent. Lenticles of

sand at higher levels were sometimes passed through and contained salt water sometimes accompanied by considerable volumes of gas (up to 200,000 cub. ft. per day).

The structure of the field was not unlike that at Sipe Springs, the beds having a gentle dip to the west. From the evidence

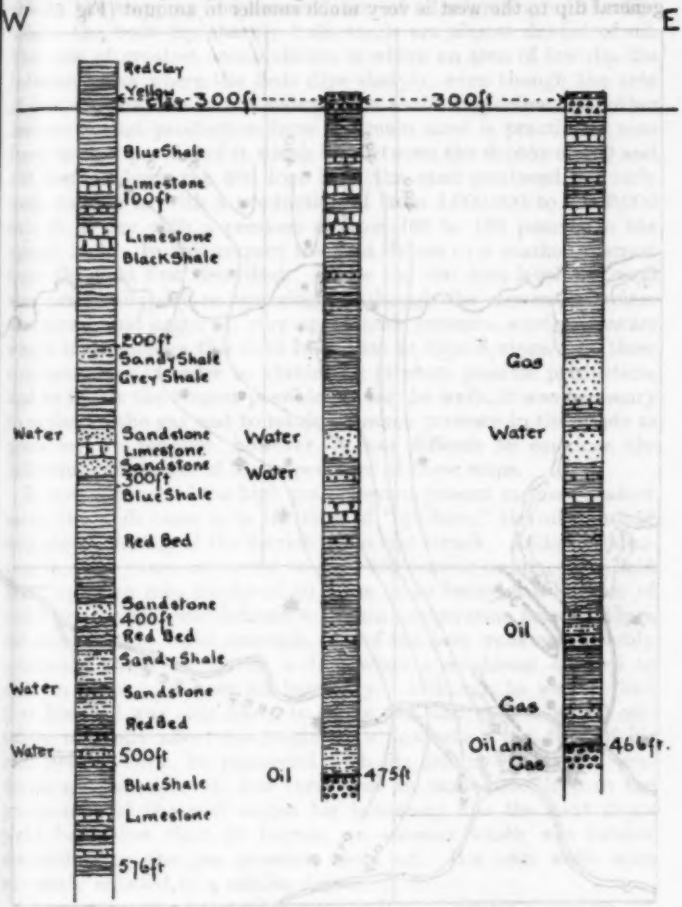


FIG. 4.

TYPICAL WELL SECTIONS ACROSS THE DEEP CREEK SHALLOW OILFIELD SHOWING DIP AND VARIABILITY OF STRATA.

obtained by drilling it was found that the strata were dipping more steeply than was evident at the surface. Contours run on the producing horizon gave dips which varied from one in five to about one in twenty. This is due to local rolling for when the beds are traced over wider areas it becomes evident that the general dip to the west is very much smaller in amount (Fig. 5).

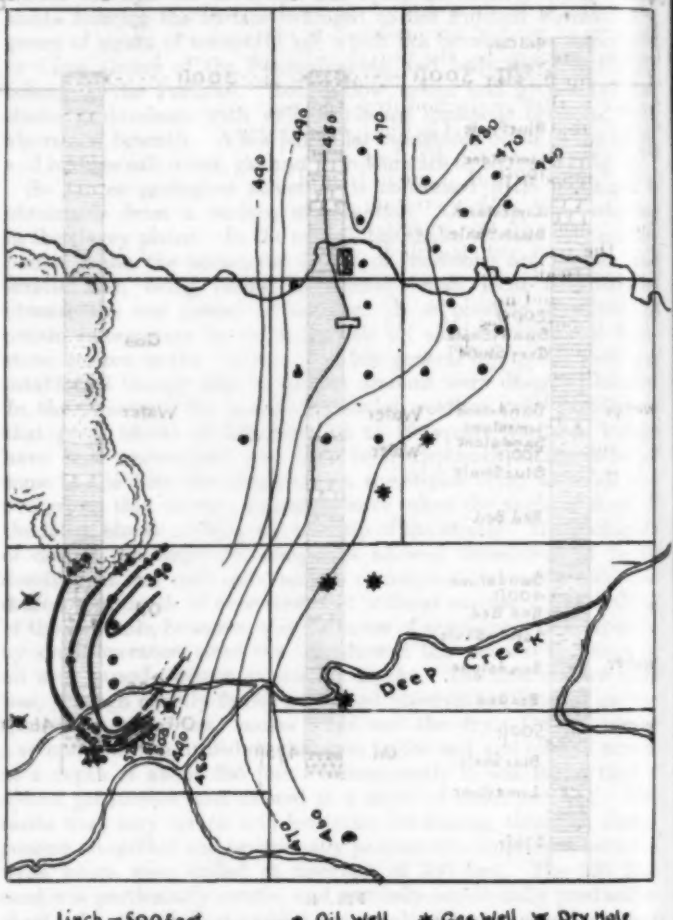


FIG. 5.

DEEP CREEK SHALLOW OILFIELD. SUBSURFACE CONTOURS ON PRODUCING HORIZONS. DEPTH BELOW SURFACE DATUM.

The running of the structural contours on the main producing horizon gave very instructive results. The strike of the beds was almost north and south, the dip being westerly. A little rolling at right-angles to the strike connected with a sharp diminution in dip resulted in the formation of terraces which have been favourable to the trapping and accumulation of oil migrating up the dip. Where the beds dip sharply both sands are almost devoid of oil. The area of greatest accumulation is where an area of low dip lies between areas where the beds dips sharply, even though the area of low dip may be of the nature of a shallow syncline. Another feature is that production from the main sand is practically confined to that portion of it which lies between the depths of 460 and 480 feet. Above the 460 foot level the sand produced gas only wells coming in with a production of from 1,000,000 to 5,000,000 cub. ft. a day with a pressure of from 100 to 120 pounds to the square inch. In this respect the field differs in a marked manner from the field first described. Below the 480 foot level the sand was practically dry or waterlogged, though the amount of water was small, and under no very appreciable pressure, another feature which distinguishes this field from that at Sipe Springs. In these circumstances in order to obtain the greatest possible production, and to insure the longest possible life for the wells, it was necessary to conserve the gas and to retain as much pressure in the sands as possible. In practice, however, it was difficult to convince the individual producers of the importance of these steps.

In consequence of the high gas pressures present in these shallow sands the wells came in in the form of "gushers," the oil spouting well above the top of the derrick when first struck. Initial production in some cases amounted to over 100 barrels a day. The field being split up into blocks of 40 acres or so between a number of small producers it was difficult to obtain co-operation between them for conservation. For example, one of the best wells was steadily producing about 50 barrels a day, when a neighbour decided to drill an offset to it near his boundary. Although he was advised that his well was only likely to strike gas, and that it would certainly not only affect his neighbour's production but that of his own nearby wells, he proceeded with his drilling. The well produced gas as expected, and there was an immediate drop in the production of the well across his boundary line the next day's yield being less than 20 barrels, an amount which was further diminished as the gas pressure eased off. His own wells were adversely affected to a similar degree.

The contouring of the oil horizon indicated clearly therefore not only where production was to be expected, but it showed the way to new areas where drilling could be undertaken with successful

results. In endeavouring to trace out the productive level of the sand to the south new levels of production were discovered, an interesting feature being that the contouring proved the existence of an unsuspected break in the shallow water deposits. Production was obtained at about 400 feet from a dome-like fold in the higher sands which overlapped the more sharply dipping lower strata. The sub-surface contouring rather suggests the presence of a reversed fault in these strata, with some overthrusting from the west.

It is perhaps unnecessary to give similar details with regard to this field, as those set out in the first part of this paper. The wells being drilled a year or two later it was possible to find contractors willing to do the drilling at $1 75 per foot, as against $3·00 per foot at Sipe Springs. The cost of equipment was very little less in proportion to depth. Wells could be drilled and equipped to 475 feet in eight to ten days at a cost of about $1500·00.

Wells were pumped by eccentric gear operating rods and wire lines from a central pumping station. The Texas Company ran its own pipelines to the field, both for gas and oil delivery being taken under gauge direct from the wells in the one case and from the operators' own storage tanks in the other. The price paid for the gas was five cents. per 1000 cub. ft., while the price obtained for the oil on the spot averaged about $2·50 per barrel. The oil was very similar in quality to that obtained at Sipe Springs.

IV.—A Comparison Between the Fields.

In making a comparison between these two shallow oil fields we find a similarity in structure and in the nature of the producing deposits. The oil has been trapped and has therefore accumulated where abrupt changes occur in a dipping porous stratum. In the first case accumulation has been greatest in small folds transverse to the strike of the beds. The second case is rather one of terracing in the dipping stratum. Beds which are dipping fairly steeply in places dip less steeply and oil has accumulated where the dip is arrested, even though the area may take the form of a depression in the stratum. It may be worth noting in this case that where the dip approximates to one in five the sand is practically dry, payable production of oil being obtained only where the dip is 1 in 15, or less. There is also a tendency for oil to accumulate locally into small pools where a bed of sand becomes constricted or near where it passes into limestone. In the first case the productive sands contain little gas and much salt water in the oil-bearing stratum. In the second case much gas under strong pressure is present and comparatively little water. The result

of this is that in the first case oil ran steadily into the wells, but there was no spectacular overflowing at the surface. In the second wells spouted as importantly as those deeper wells, so attractive when pictured in the literature of oil finance, known as "gushers."

It is difficult to make a fair comparison between the "lives" of wells in these two fields. The evidence indicated that the wells in the second field would not produce half as long as those in the first. It frequently seems to be the case that where the flow of oil in the well depends upon hydrostatic pressure the wells produce for longer periods than where gas pressure is the important factor. In the latter condition as much or more oil may be produced, but it is forced out of the sands more quickly, and the stage of exhaustion comes in a shorter period of time as would be expected. But there is another factor. It is easy for the operator to destroy his gas pressures. He can use the gas under his boilers or for general heating and lighting purposes, sell it to pipeline companies or run it to waste which he often does. He is not interested in the salt water that may be present in the beds excepting to avoid it if possible. It is difficult to persuade him that really there is no reason why oil should run to any extent into his well from its porous container if the gas or water pressures were eliminated. So although the life of the wells in the second field showed signs of being short it is difficult to know what it would have been had gas pressure been maintained and conserved. It is also difficult to estimate in such cases how much oil remains in the sand when the pressure has been run off to such an extent that production has practically ceased. Cases are known in the United States where fields have been abandoned for some years and yet when redrilled by an adventurous spirit have proved productive again. This has been due to a rejuvenation in gas pressure in the oil sands during the years when the field has been idle. Nature has got to work again, further accumulation of gas and oil in favourable spots has taken place, and to some extent the old damage has been remedied. Both production and the productive areas are certainly smaller, but with scientific care both during exploitation and in the abandoning of wells, there is reason to believe that many old oil-fields would become productive again after a few years of rest.

Although the two oilfields under consideration are producing from different groups of the Pennsylvanian Formations of Texas, there is a remarkable similarity in the chemical constitution and the physical properties of the petroleums obtained. This similarity has been noted not only in widely separated oilfield areas in this part of the Mid-Continental oilfield region, but in producing horizons which range almost from top to bottom of this important system. It may be that the petroleum present

in these different horizons has originated from some common mother source, say, in the underlying Bend Group, from which there has been very extensive migation. Faulting may have played an important part in such migration, and there is reason to believe that petroleum which is being obtained from sands which occur in formations much younger than the Pennsylvanian may have come from the same source. Faults are important features in the structural conditions connected with oil accumulations in Eastern Texas, and in the neighbouring parts of Louisiana, and may indicate the means and direction of migration. I hesitate to make more than the suggestion, but there is evidence to support such a view.

DISCUSSION.

Mr. E. H. Cunningham Craig, in opening the discussion, thought the paper was very instructive. Those geologists who were accustomed to fields in which the strata dipped at fairly good angles and in which there were most distinct anticlines and domes did not encounter such curious conditions as obtained in fields such as those described in the paper where the dips were very gentle. The reason, he supposed, was that the more gentle the dip the more the effect obtained from friction in the oil sands; while the head of water and the head of oil had considerable effects very different from those obtained in steeply dipping strata. Questions also arose in connection with whence the oil came, the direction of migration of the oil and also the direction of migration of the water. If the strata were not very porous, and there was no great head of water tending to force the head of oil in one direction, it stood to reason that most abnormal relations could be obtained between the water and the oil, so that it was necessary to study with the very greatest care the terraces and the curious contours that were illustrated in Dr. Wade's paper. In the ordinary fields with which so many of the members dealt, where there was a really good dip and a well-defined anticline, such extraordinary incursions of water were not obtained along irregular lines. They were accustomed to get an edge water which came in fairly regularly, unless, of course, there had been a very large production in one part of the field which brought in the water more quickly. There was another point that Dr. Wade had brought out very clearly—namely, that if a field was left alone in the course of a few years a different equilibrium was set up, so that, although water might have been brought in and the wells abandoned, after the field had been left for some time the oil might come back again when an equilibrium was established once more.

Mr. T. Dewhurst said that the paper was not only interesting, but also important, as the author's description of two small fields

enabled one to see in operation several important principles in connection with the development of oilfields. In big fields the changes that went on underground were usually so slow that it was difficult to realise not only their significance, but even their existence, whereas in small fields such as those described by the author the lessons were brought out strongly and clearly. During the past few years a great deal of attention had been paid to the question of the conservation of gas in oil sands, and the importance of this principle was illustrated by the case of the Deep Creek field, which was fully described in the paper. The oil in that field was forced into the wells by means of gas pressure, and as the author had pointed out, it was most important that as much gas as possible should be conserved in the oilsands so that the maximum benefit of the gas pressure could be utilised in bringing the oil into the wells. It was a very easy matter to effect, and a difficult one to avoid, very rapid reduction of gas pressure in an oilfield, with the result that a large proportion of the oil was left in the sands and would not migrate to the wells in paying quantities. In this way enormous quantities of normally irrecoverable "dead" oil were left underground in the oilsands. Numerous estimates had been published in petroleum literature during the past few years to the effect that 60, 70, 80 per cent. and perhaps even more of the oil in an oilfield remained underground in that condition simply because the gas had been dissipated and there was no force left to drive the oil into the wells. Doubtless, in the course of time, as had been pointed out, a process of rejuvenation took place, and although it seemed reasonable that this would occur, it would nevertheless be of great interest to members if the author, either now or in his written reply, would give some particulars of cases in the United States where rejuvenation had taken place. Any such rejuvenation that had occurred was doubtless due to the edge water. There was a lag between the rapid loss of gas pressure and the slow effect of the edge water in readjusting the fluids underground and restoring more or less the former balance, but gradually the enormous amount of oil left in the sands was forced by edge water to occupy a smaller area, finally producing a smaller resuscitated field. The importance of the edge water was clearly illustrated by the Sipe Springs field, and Fig. 2 of the paper showed the incursion of edge water along the synclinal depression. The final sentence of the second paragraph dealing with the encroachment of water on the field was of great interest and was well worth repeating. "The presence of the water and its movement up the dip of the beds is, therefore, probably very advantageous to the wells which are high on structure and must be regarded as a favourable factor so far as ultimate production is concerned."

A further important point was the bearing of the movement of edge water on the curves given in that part of the paper dealing with the valuation of oilfields. In wells which were situated low on the structure it was most probable that the water would encroach and drown the oil at an early stage in the history of the wells, whereas wells situated high on the structure would probably go on producing for very long periods indeed. Those facts would probably affect very greatly the estimates based on the extension of production curves of the quantity of recoverable oil left in a field, and he would like the author to deal with this point in his reply. In any case, it was only possible for a geologist to make a rough approximation of the future life of a field. Those engaged in the more exact sciences were more favourably placed, as after they had applied their exact science to practical problems and had worked out results with meticulous accuracy, they were in the habit of applying a safety factor of two, three or more as the case seemed to require. The geologist could not adopt that convenient device; all he could do was to give a rough approximate result which, nevertheless, was most valuable and useful. In regard to Fig. 1A, showing the correlation of well records, it was a suspicious circumstance that there should be limestone in Wells Nos. 1 and 3 and none in the corresponding position in Well No. 2 situated between them. This result might be due to careless logging on the part of the driller and perhaps should not be treated as being proof of rapid lateral variation of the strata.

Dr. Wm. Hope Henderson said the author referred in his paper to the tendency of large companies intentionally to ignore shallow oil horizons. That policy seemed to be natural because usually shallow-oil was "poor man's territory," yielding excellent profits at very low costs on small or limited production and due to the personal element when operated by interested individuals. Large companies, knowing shallow oil to exist and such oils thus safely stored for the future, but uncertain of deep-oil, were frequently forced to purchase areas outright so as to keep the annoying small operator from spoiling possible reserves, but might then lease for shallow production only.

The value of shallow-oil was so variable that estimates were sometimes most unreliable. He knew of a case, among others, in which a few drillers secured a lease of 120 acres from a large operating company and with a total capital of $10,000 drilled 79 post-hole wells, all from 50 ft. to less than 200 ft. in depth, and obtained such good production of high quality oil that within a year they sold out for a million dollars. The large company had leased only a small part of their large tract of land and had known of the shallow-oil horizon for many years from the evidence of

outcrop sands, but the quantity and quality of the oil was unknown and they did not require nor desire to develop it themselves at that time, because such organisations do not want to be bothered with what are probably small shallow fields.

The author referred to a costly well sunk to more than 4,000 ft. in depth without success and seemed to indicate that the geologists advising the company were somewhat at fault in sinking the well so deep. Personally, however, he thought such pioneer wells were of extraordinary value in connection with subsequent work on the fields. The Spur Well (4,489 ft.) in Dickens County was a notable example of this and had given information of incalculable benefit to all, therefore he thought the well in question had been a valuable guide. Certainly the geologists, by means of that well, had evidently discovered the shallow horizons and had saved other people from doing similar testing for the time being. The well might quite reasonably have struck oil in any of those (elsewhere) productive formations. He thought, in general, when oil was not found where it was anticipated in a well and oil formations continued, the geologist usually advised carrying on to greater depths so long as the going was good and the company could afford the expense.

He noticed the author had given an example of a typical valuation of a lease, assuming the wells would be drilled by the producers, and the net value of the lease was $98,844. Was that rough valuation the basis on which the owner and the operator would bargain, as there seemed to be other factors to be considered before any purchaser would agree a price.

At the end of the paper the author referred to the important question of migration, which was a theory demanding a great deal of latitude. There were some extremes in granting vertical migration up or down, and in suggesting that the oil had to travel for many miles until it found some other outlet, such as a suitable unconformity or fault; and although it had been perfectly accommodated in its original home for ages prior to deposition of later formations, it must, in order to suit the theory, migrate over considerable distances, and instead of dispersing become accumulated in certain beds where it was now found. That did not seem in many cases to be quite reasonable, because in production methods it was extremely difficult to extract even 20 to 50 per cent. of the petroleum from the oilsands; and yet those beds from which the oil had migrated did not often contain quantities of oil. Much, he thought, depended on the views entertained with regard to the origin of oil, and he believed that Mr. Colin C. Rae's paper on "A Possible Origin of Oil," which dealt chiefly with the colloids of the humus acid groups, was worthy of more serious consideration.

Was it not possible that this theory, if carried to its logical conclusion, might satisfy many arguments in regard to the primary depositional origin of petroleum whether in sand, limestone or shale. The basis of consideration presupposed the existence of oil or its mother substances derived from any sources, continental or marine, and the protection thereof by gels and the like of coagulations, both organic and inorganic, which carried by prevailing currents laden with comminuted mineral matter would be deposited and the gels redispersed or peptised, leaving the oil content to adjust itself in the deposit and form into the varieties of petroleum now found according to the conditions of deposition and the original substance involved.

Mr. C. Dabell said that in the diagram showing the encroachment of the water he was rather surprised to find that the water was encroaching along the strike, leaving the wells both up the dip and down the dip untouched. He could quite understand why the wells up the dip were left untouched by the water, but it was difficult for him to appreciate why the wells down the dip were also left untouched.

Mr. Alexander MacDougall thought it would be of interest if the author would give some idea, from observations that had been taken in various wells, of the distance the oil was supposed to migrate. Geologists said that a disused well existed in a particular place and a producing well in another place; then suddenly the disused well came into operation, oil being found in it. What was the average distance the oil travelled, and what was the difference in level between the two points?

Mr. W. H. Fordham said the President had reminded the members that the present was the hundredth meeting of the Society, and it seemed to him a pity to allow the occasion to pass without some reference to the first paper read at the first meeting of the Institution. The paper was on "The Geometrical Properties of the Anticline," by Sir Thomas Holland, the President, and he thought reference to that paper would do a great deal to solve the question asked by Mr. Dabell.

Mr. R. J. Ward said he was particularly interested in the conclusions arrived at by the author in reference to the use of water in increasing production, which appeared to him to be on a par with the flooding experiments which were now being made in one of the fields at Bradford, Pennsylvania, by the Petroleum Reclamation Company. In that case water was being utilised to compress the gas to push the oil along, and by a series of rows of water wells and oilwells the production was being increased. During last summer he met various officials of the Bureau of Mines and became interested in some experiments which they had recently been

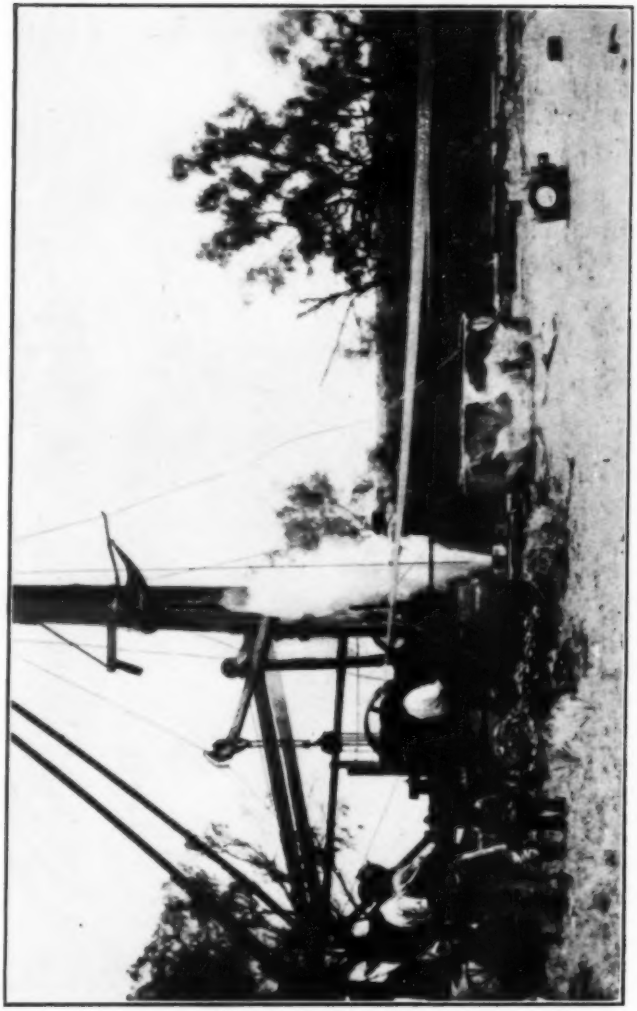
carrying out on one of the oilfields at Davenport, Oklahama. Most petroleum technologists who were used to production methods on the fields had a bogey known as "back pressure." The method adopted on the field he had mentioned was to utilise back pressure, but the term not being liked they called it "control pressure." They were able to prove to the companies that, by controlling the pressure on the sands, they were able to increase their production, and the wells also had a longer life.

Mr. Gordon Pitt said there were two small points, one of a non-geological nature, and the second relating to a point raised by a recent speaker, on which he wished to remark. He would like a little more information, if possible, about the well that was drilled to a depth of 200 ft. for a cost of 400 dollars. The other point referred to a question mentioned in the paper and also by a recent speaker—namely, rejuvenation. He came across a rather extraordinary illustration of rejuvenation in Trinidad some years ago. A particular well had been drilled in the very early days of development in Trinidad which had quite distinctly penetrated the oil sand. He forgot the exact depth, but it must have been somewhere in the neighbourhood of 1,300 to 1,400 ft. The well was a small uneconomical producer, but it served the useful purpose of locating the exact depth of the oil horizon at that particular spot. The well had been kept open and either baled or pumped at infrequent intervals until the time arrived when, about 700 or 800 yards away from it, a very spectacular gusher was brought in which, at that particular time, was claimed to be the world's most prolific producing well. It was rather unfortunate, he thought, that out of the 80,000 or 90,000 barrels it was said to give in the first twenty-four hours not more than 80 or 90 barrels were recovered. The well came in with an amazing pressure sufficient to damage the derrick and to flow for a considerable number of hours with a very large production which was lost. The well sanded up to a certain extent, and it was decided to cement it with a view to redrilling through the cement. It was duly cemented up solid, but it was not brought into production again. The well 700 or 800 yards away, to which he had previously referred, since the gusher came in had produced no oil whatever. It had been baled at intervals for a time but gave no production at all. But about a year later gurgling noises were heard coming from it. He endeavoured to discover what was happening down below and found that 40 or 50 ft. of sand had been forced up into the well. He cleaned it and recovered from that well, from exactly the same depth as that from which it previously came, more oil than was originally produced from it. That was a specific example of the rejuvenation of an oil well.

The President, in conveying the thanks of the Institution to the author for his interesting paper, said the discussion had shown that the paper was practically complete in itself. The author had given a very complete and simple object lesson worked out from every point of view in a way which was characteristic of the previous work he had done. Many of the points raised in the discussion were of a kind that were answered within the paper itself, and he thought the author would confirm that view. The point, however, raised by Mr. Dewhurst was apparently not discussed fully in the paper—namely, the variations in the lives of the wells as estimated for revenue purposes. The variations seemed to depart seriously from the type curve shown. There was one other feature to which he would like to refer of which no mention was made in the paper. In a field like that described by the author, so uniform in character and drilled so thoroughly, but possessing at the same time such lateral variations in the lithological characters of the beds, he would have expected some evidence to answer the question whether there was any mutual influence between adjacent wells; whether any of the wells influenced the production of their neighbours or whether it was found that the discontinuity of the beds was accompanied by an independence in production. He desired to thank Mr. Fordham for referring to the first paper read at the Inaugural Meeting of the Institution. He wished that Sir Boverton Redwood were present to celebrate the one hundredth meeting, and to realise, as all those present did, that they had listened to a paper that was up to the standard that the Institution had attempted to maintain throughout its history.

Dr. Arthur Wade, in reply, said Mr. Dewhurst had asked whether he could give any instances of fields in the United States which had been rejuvenated. He knew personally of areas in the old Pennsylvanian tract which had been redrilled within recent years. Some of the very oldest producing areas had been drilled again and had become productive. Successful drilling in some of the older fields in Texas seemed to indicate rejuvenation in these areas. With regard to the production curves that had been shown, it was true that different conditions produced different curves. Curves obtained in different parts of the Sipe Springs field showed different characteristics, variations being due to the nature of the variable factors present, such as pressure. In some cases there was no sharp fall during the period of flush production, and in consequence no sharp change between the portions of the curve representing flush and settled production. In other cases the change between flush and settled production was even more pronounced. The curve shown was selected as being about an average

SHUTTING OFF A "GUSHER," DEEP CREEK.



RUNNING OUT GAS, DEEP CREEK

one for the field. There was a distinct difference in the curve between a well which depended on water pressure and one which depended on gas pressure. Mr. Dewhurst had drawn attention to the absence of limestone in one of the sections shown in the diagram. He (the author) had pointed out when dealing with the section that the wells were not quite in line. In all probability a re-entrant angle or curve was present in the margin of the limestone and in this re-entrant angle one of the wells had been drilled. Something of that nature had certainly taken place. The section was not altogether dependent upon the driller. As a matter of fact the same driller drilled the three wells and would expect to find the same thing in every one.

In reply to Dr. Henderson's remarks he wished to say that he did not find fault with the depth to which the well in question was sunk—namely, 4,000 ft.—but with the geology upon which the well was located. He simply drew attention to the fact that, from a geological point of view, the site was a bad one. He quite agreed with Dr. Henderson that the well proved to be most useful. It provided quite a lot of information and led to the development of shallow oilfields. At the same time it was an expensive way of doing this.

Some of the points that had been raised were dealt with in the paper itself, and Mr. Dabell's point had been thoroughly answered by Mr. Fordham's remarks. The depression along which the water was encroaching was in the form of a gutter along the flanks of dipping strata, very much the same thing as a gutter along the side of the roof of a house.

The point raised with regard to the distance that oil was supposed to migrate was a very difficult one, into which there was not sufficient time to enter that evening. The economical spacing of oil wells was supposed to be based to some extent on the distance to which oil could migrate into a well; but there were a good many features in connection with the more general question of migration which it would take a whole paper in itself to discuss. The suggestion had been made that back pressure should be used in the wells. In the Deep Creek field, after the pressure had been let off a half-hearted attempt was made to put on back pressure, but it was not very successful.

A question had been asked with regard to a statement in the paper that a 200 ft. well cost only 400 dollars to drill. As a matter of fact the well was slightly less than 200 ft. deep. The amount stated was that spent in drilling the well. Probably nothing in the way of equipment was included in the figure. Contract drilling at $2 a foot is not unknown in the shallow oilfields even in development which has taken place since the war.

The President had referred to the influence which a well might have on its neighbours. It was quite certain that production from one well did affect that of other neighbouring wells. He had given an instance in the paper of a newly-drilled gas well which so affected a neighbouring oil well as to reduce the production to less than half in one night. The operator had been told that it would not be advisable to drill this well, because not only would it damage his own wells, but the wells of his neighbours also. That was a very serious state of affairs, because in such cases production was perhaps irretrievably lost. In small wells where the sands were very lenticular the production stood up pretty well as a rule in spite of oxset drilling. The drilling of offset wells sometimes did not affect them in any way. He knew of one case where a productive shallow well was offset in four directions by others which were quite dry owing to the thinning out of the sand. The maximum quantity of oil was obtained if the gas pressure was slightly conserved, but it was not advisable to start drilling at 50 ft. spacings to try and get all the oil out of the sand. He had met with one producer who, instead of being satisfied with the production that could be obtained by a scientific spacing of wells based on practical experience, drilled others a few feet away from the discovery well, with the result that the field was damaged, little or no production was obtained and the initial well was ruined.

(The Meeting then terminated.)

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

ANNUAL REPORT OF THE COUNCIL FOR 1926.

IT is with pleasure that the Council present their Annual Report for the year ended December 31st, 1926, together with the Accounts.

During 1926 the total net increase in membership was 92, as compared with 67 in 1925, and the following table shows the total in each class on December 31st, 1926, and the changes during the year :—

	Total 31.12.25.	Changes during 1926.							Total 31.12.26.
		New.	Transferred to.	Re-signed.	Deceased.	Removed.	Transferred from.	Net gain or loss.	
Honorary Members	10	—	—	—	—	—	—	—	10
Members	403	30	4	3	3	—	—	+28	431
Associate Members	221	49	14	4	1	—	4	+54	275
Students	120	15	—	2	—	—	15	— 2	118
Associates ..	42	16	1	4	—	1	—	+12	54
Totals ..	796	110	19	13	4	1	19	+92	888

In addition to the above, 26 members, recently elected, had not, at the end of the year, taken up their election and 29 prospective members were awaiting election.

The Accounts for the year ended December 31st, 1926, are presented, and Council are glad to state that the Balance Sheet continues to show a satisfactory financial position.

The Scholarships awarded by the Institution have been provided for in the Accounts, and it has been decided to continue the Awards for the year 1927.

The sum of £400, which has been allocated from the General Funds for the purpose of providing grants in connection with special Research Work, has been dealt with in accordance with the regulations laid down by the Institution. The operation of this Fund is shown in the Accounts.

The Institution is represented on :—The American Society for Testing Materials; the Advisory Board of the Department of Oil Engineering and Refining of the University of Birmingham; the British Association for the Advancement of Science; the

British Engineering Standards Association; the Fuel Economy Committee, and the Imperial Mineral Resources Bureau. Official representatives of the Institution were also present on the Home Office Committee appointed to consider and revise Flash-Point Apparatus; the International Electrotechnical Commission, New York, April, 1926; the Annual Meeting of the Congress of Chemists, London, July, 1926; the Smoke Abatement League of Great Britain, Birmingham, September, 1926; the 5th International Road Congress, Milan, September, 1926; the 6th Congress of the Société de Chimie Industrielle, Brussels, September-October, 1926; and the International Conference on Bituminous Coal, November, 1926.

Eight General Meetings of the Institution were held during 1926, and the following papers were read and discussed:—

Ninetieth General Meeting, January 12th: "THE VAPOUR PRESSURES OF FUEL MIXTURES, PART II.," by J. Stanley Lewis; "SYMPOSIUM ON THE ESTIMATION OF UNSATURATED HYDROCARBONS."

Ninety-first General Meeting, February 9th: "THE SULPHUR COMPOUNDS OF KIMMERIDGE SHALE OIL," by Frederick Challenger, John Haslam, Randle James Bramhall and James Walkden.

Ninety-Second General Meeting, March 9th: "THE SEARCH FOR OIL IN AUSTRALIA," by Arthur Wade.

Thirteenth Annual General Meeting, March 23rd: PRESIDENTIAL ADDRESS, by Sir Thomas H. Holland.

Ninety-Third General Meeting, April 13th: "THE OILFIELDS OF THE MARACAIBO BASIN," by Campbell M. Hunter.

Ninety-fourth General Meeting, May 25th: "ORGANIC THEORIES OF OIL ORIGIN," by Ernest Clark.

Ninety-fifth General Meeting, October 12th: "THE SIGNIFICANCE OF SURFACE OIL INDICATIONS," by A. Beeby Thompson.

Ninety-sixth General Meeting, November 9th: "OIL FUEL AND OTHER FUELS FROM CARBONIZATION PROCESSES," by F. Mollwo Perkin.

Ninety-seventh General Meeting, December 14th: "A CONTRIBUTION TO THE STUDY OF THE ORIGIN OF PETROLEUM: THE BERGINISATION OF FISH LIVER OILS AND OTHER BODIES," by W. R. Ormandy, E. C. Craven, I. M. Heilbron and H. J. Channon.

Six numbers of the Journal were published during the year, and contained, in addition to the above-mentioned papers, a number of others dealing with the technology of petroleum. The Decennial Index to the first ten volumes of the Journal was also published and made available to members of the Institution at cost price.

The London and Birmingham Branches of the Students' Section report that during 1926 they have each held eight Meetings, at which papers dealing with various aspects of the Petroleum Industry have been read and discussed.

Mr. Alfred C. Adams has been unanimously elected President for the ensuing year.

The Rt. Hon. Viscount Cowdray of Cowdray, Sir John Cargill, Mr. Alexander Duckham, Mr. Arthur W. Eastlake, Mr. Robert Redwood and Dr. W. R. Ormandy have been unanimously re-elected Vice-Presidents for the ensuing year.

The Students' Medal and Prize for the 1925-6 Session has been awarded to Mr. Harvey S. Garlick for a paper on "The Scottish Shale Oil Industry." The two Scholarships were awarded to Mr. William Edmund Madden at the Royal School of Mines and to Mr. Guy Tunstall Notley at Birmingham University respectively.

The Library Committee report that, during 1926, 60 books (including bound periodicals) were added to the Library, making the total number of books 1,265. In addition, 160 papers, pamphlets and catalogues were received, together with a number of unbound periodicals, general papers and maps. A Lending Library has been formed for the use of Student Members, and a total of 135 books are available for this purpose. It is estimated that during the year about 300 persons consulted the Library, either by personal visits, correspondence or telephone, this being a considerable increase over the previous years.

Arrangements are being made for the formation of branches of the Institution in other countries, where there are sufficient resident members to warrant this. One such branch is in active course of formation in Rumania and one is contemplated in Persia, and it is hoped that they will be definitely established early in 1927.

The Council have decided that the sum of £400 is to be allocated annually to the advancement of Research in Petroleum Technology and its basic sciences, and the first amount has been provided in 1926.

The Standardization Committee is continuing its activities, and it is expected that during the forthcoming year the book of Standard Methods will be issued in a revised form to include amended and new methods.

The eighth Annual Dinner was held on March 26th, 1926, and attended by over 200 members and guests. It has been decided that in future the Annual Dinners shall be held towards the end of the year in preference to the beginning. On October 5th, 1926, a Conversazione took place at Aldine House, and was attended by over 120 members and friends.

It is with great regret that the Council have to announce the decease of four members: H. R. Berry, W. C. Carter, C. W. Watson and J. E. Miller.

The Council desire to express their appreciation of, and thanks to, the Royal Society of Arts for their continuing to allow the Institution the use of their House for Meetings, and to the Chemical Industry Club for permitting the use of their premises by the Dinner Club.

The Council also wish to record their appreciation of, and thanks for, the services rendered to the Institution by:—Sir William Plender, Bart., G.B.E., Honorary Treasurer; Messrs. Ashurst, Morris, Crisp & Co., Honorary Solicitors; Messrs. Price, Waterhouse & Co., Auditors; Dr. A. E. Dunstan, Honorary Editor; Mr. George Sell, Assistant Editor; and to the Secretary, Commander R. E. Stokes-Rees, R.N., and his Staff.

The Auditors retire and offer themselves for re-election.

By Order of the Council,

ARTHUR W. EASTLAKE,
Honorary Secretary.

REVENUE ACCOUNT for the year ended 31st December, 1926.

Dr.	£	s.	d.
To Salaries	952	2	8
„ Rent, Rates, etc.	448	4	9
„ Printing and Stationery	166	9	9
„ Postage	145	3	3
„ Hire of Hall for Meetings and Expenses of Meetings	195	4	6
„ Journals	334	12	8
„ Income Tax on Interest and Dividends paid without Deduction	16	8	0
„ Auditors' Fee	10	10	0
„ Students' Prize and Scholarship Fund	80	0	0
„ Research Fund Account	400	0	0
„ Sundry Expenses	272	12	7
„ Depreciation of Office and Library Furniture and Library Books	55	18	11
	3077	7	1
„ Balance carried to Balance Sheet	161	4	2
	£3238	11	3

Cr.	£	s.	d.	£	s.	d.
By Subscriptions—						
Members	2151	9	0			
Special	901	5	0			
				3052	14	0
„ Interest and Dividends				139	6	7
„ Sale of Books				46	10	8
				£3238	11	3

STUDENTS' SECTION FUND.

1926.		£	s.	d.
Dec. 31.	To Expenses for the Year	16	12	11
	„ Balance carried forward	58	10	3
		£75	3	2

1926.		£	s.	d.
Jan. 1.	By Balance brought forward	75	3	2
		£75	3	2

STUDENTS' PRIZE AND SCHOLARSHIP FUND.

1926.		£ s. d.	£ s. d.
Dec. 31.	To Scholarships granted—		
	Royal School of Mines	40 0 0	
	Birmingham University ..	40 0 0	
			80 0 0
	„ Special Prize awarded		5 0 0
	„ Balance carried forward		15 0 0
			£100 0 0
1926.			
Jan. 1.	By Balance brought forward		20 0 0
Dec. 31.	„ Revenue Account		80 0 0
			£100 0 0

RESEARCH FUND.

Dec. 31.	To Grants during Year for Research Work ..	35 0 0
	„ Balance	367 15 2
		£402 15 2
Dec. 31.	By Revenue Account	400 0 0
	„ Interest	2 15 2
		£402 15 2

BALANCE SHEET as at 31st December, 1926.

LIABILITIES.

	£ s. d.	£ s. d.	£ s. d.
To Capital of the Institution, under Bye-Law Section 6, para. 14, *viz.*:—			
Life Membership Fund, as per last Account		413 0 0	
Entrance Fees—			
As per last Account	1116 2 0		
Additions during year	151 4 0		
		1267 6 0	
Donations per last Account ..		326 5 0	
			2006 11 0
„ Students' Prize and Scholarship Fund			15 0 0
„ Research Fund Account			367 15 2
„ Students' Section Fund			58 10 3
„ Subscriptions Paid in Advance ..			149 2 0
„ Sundry Creditors			365 1 0
„ Revenue Account—			
Balance at 31st December, 1925 ..		1850 15 8	
Less: Arrears of 1925 Subscriptions written off		49 7 0	
		1801 8 8	
Add: Balance for year as per Revenue Account		161 4 2	
			1962 12 10
			£4924 12 3

ASSETS.

	£ s. d.	£ s. d.
By INVESTMENTS AT COST—		
(1) On Account of Capital—		
£664 6 6 London County 3% Consolidated Stock	481 10 6	
£925 0 0 5% War Loan, 1929/47 ..	862 18 4	
£50 0 0 National War Bond 5%, 1927 ..	50 0 0	
£150 0 0 Birmingham Corporation Stock 6%	146 16 0	
£515 1 9 Conversion 3½% Stock	400 0 0	
		1941 4 10
(Note: Market price of above Investments at 31st December, 1926, was £1938 7s. 10d.)		
(2) On Account of Revenue—		
£500 0 0 5% War Loan, 1929/47 .. (Market value, £503 15s. 0d.)		501 19 6
„ RESEARCH FUND INVESTMENT ACCOUNT—		
Cash on Deposit with Bank		367 15 2
„ OFFICE AND LIBRARY FURNITURE (excluding presentations)—		
As per last Account	487 12 4	
Less: Depreciation	24 7 7	
		463 4 9
„ LIBRARY (BOOKS) (excluding presentations)—		
As per last Account	178 7 10	
Additions during year	32 1 0	
	210 8 10	
Less: Depreciation	31 11 4	
		178 17 6
„ SUBSCRIPTIONS (1926) OUTSTANDING at date and considered collectible		66 13 6
„ SUNDRY DEBTORS AND PAYMENTS IN ADVANCE..		196 13 10
„ CASH ON DEPOSIT		986 13 8
„ CASH AT BANK AND IN HAND		221 9 6
		£4924 12 3

T. H. HOLLAND,
A. DUCKHAM, } Members of Council.

We have examined the above Balance Sheet with the books of the Institution, and having obtained all the information and explanations we have required, we are of the opinion that such Balance Sheet is properly drawn up as to exhibit a true and correct view of the state of the Institution's affairs, according to the best of our information and the explanations given to us and as shown by the books of the Institution.

PRICE, WATERHOUSE & Co.

3, FREDERICK'S PLACE,
OLD JEWRY, LONDON, E.C. 2.

25th January, 1927.

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE FOURTEENTH ANNUAL GENERAL MEETING of the Members of the Institution was held at the House of the Royal Society of Arts, John Street, Adelphi, London, W.C. 2, on Tuesday, March 22nd, 1927. Sir Thomas Holland, K.C.S.I., the retiring President, took the Chair.

The Secretary (Commander R. E. Stokes-Rees, R.N.) read the notice convening the meeting and the Minutes of the 13th Annual General Meeting held on Tuesday, March 23rd, 1926, which were confirmed after a verbal correction.

The President: The list of members elected during 1926 were laid on the table, and the Secretary read the following list of members elected since the last general meeting.

Members.—Charles Henry Sanders Edmonds, Charles K. Francis, Christianus Lieshout, Arthur Moore, Pedro Roth.

Transferred to Member.—Frank Levy.

Transferred to Associate Member.—Wilfred Crompton, George Ormsby Higgins, Harry Temple Watts, Cedric Clark Wilson.

Associates.—Edgar Atkinson, William Ronald Penrose Hodgson, Harry Collins Potts, Ernest Reginald Tidey.

The President: On behalf of the Council I move the adoption of the Annual Report for 1926. From the point of view of the Council it appears to be a satisfactory report. We have had an increase of 92 members this year against an increase of 67 last year. We feel that the Institution is growing satisfactorily in numbers, having regard to the care which is being taken by the Council in admitting only those who are qualified and suitable. The total number of members at the end of 1926 was 888; since then 22 new members have joined, making our total to-day 910, so that we shall probably before the end of the year be approaching a membership of 1,000.

I move "that the Annual Report of the Council be adopted."

Sir Frederick Black, K.C.B., B.A. (Past-President): Mr. President and Gentlemen,—Like the President, I feel that this Report is so good that it does not need many words to commend it. It might be thought that a Member of Council speaking on this subject is dealing with the efforts of the Council only, but of course that is not the case. The Annual Report comprises work that has been done by the whole Institution, to which many members have contributed besides those who happen to serve

on the Council. I want to draw your special attention to the last page of the Report, and desire to mention two or three of the paragraphs referring to various activities of the Institution. First of all there is the standardisation of tests. We are hoping to bring out a new book during the forthcoming year dealing with that subject. Next there is the engagement of research work. Lastly, I should like to refer to the formation of branches of the Institution. I do not know whether that subject comes before us in any other way to-night, but, as the report states, one branch has been formed in Rumania and another is in process of formation in Persia, and we hope that others will follow. I have very great pleasure in seconding the President's proposition that the Report be adopted.

The resolution for the adoption of the Report was then put and carried unanimously.

The President announced that the Annual Report of the Students' Sections would be printed in the Journal in the usual way.

ANNUAL REPORTS OF THE STUDENTS' SECTION.

LONDON BRANCH.—The following Student Members were elected to serve on the Committee at the Third Annual General Meeting: Messrs. E. Clark, T. G. B. Davies, B. Dashkevitch, P. Driver, J. B. Kay, W. E. Madden, R. E. Palmer, W. B. Rowntree and J. O. Tanner.

Mr. Clark was subsequently elected Chairman and Mr. Kay continued as Honorary Secretary until he left England for South America in October, Mr. C. F. C. Moore being elected to fill the vacancy.

During the year eight General Meetings have been held :—

January, 1926.—"Burmese Reminiscences," by W. Crompton, A.R.S.M., Stud.Inst.P.T.

February, 1926.—Third Annual General Meeting. Lantern Lecture on "The London Omnibus: its Origin, History and Development," by H. S. Garlick, Stud.Inst.P.T.

March, 1926.—"Electrical Methods of Prospecting for Oil," by J. O. Tanner, B.A., Stud.Inst.P.T.

April, 1926.—"Lubrication," by S. E. Bowrey, B.Sc., M.Inst.P.T.

June, 1926.—"The Essential Qualities of Various Petroleum Products," by W. B. Rowntree, Stud.Inst.P.T.

October, 1926.—"Conditions Governing the Occurrence of Oil in Burma," by L. Dudley Stamp, B.A., D.Sc., F.G.S., A.K.C., A.M.Inst.P.T.

November, 1926.—Discussion on "The Economic Relationships of Oil and Coal," introduced by a paper by E. Clark, Stud.Inst.P.T.

December, 1926.—Joint Meeting with the Graduates' Section (London Branch) of the Institution of Automobile Engineers. "Factors affecting Internal Combustion," by C. I. Kelly, M.Sc., A.I.C., F.C.S., A.M.Inst.P.T.

The attendance at meetings has remained disappointingly small. This subject was brought to the notice of members in a circular letter, suggesting the discontinuance of the notification of Students' Meetings other than that which appears on the cards announcing General Meetings. The consensus of opinion appeared to be that separate notices were unnecessary and they are now only posted for special meetings.

The meeting held with the Graduates' Section of the Institution of Automobile Engineers was the first Joint Meeting to be held, but the number of Students who attended was disappointingly small. It is hoped that other joint meetings with this kindred Society will be arranged in the future.

No excursions have been arranged during the year, some difficulty having been experienced in obtaining permission to visit works. However, it is hoped that it will be possible to arrange visits during 1927.

The Council of the Institution have awarded the Medal and Prize for the best Students' paper presented during the year to Mr. H. S. Garlick, and the Scholarship at the Royal School of Mines to Mr. W. E. Madden.

In conclusion, the Committee desires to mention its sincere appreciation of the interest in the Section which has been manifested by Senior Members throughout the year.

(Signed) CHARLES F. C. MOORE,
Hon. Secretary.

(Countersigned) T. H. HOLLAND,
President.

BIRMINGHAM BRANCH.—The Committee have much pleasure in presenting the Fourth Annual Report for the year ending December 31st, 1926.

The average number of members of the Branch was twelve and the average attendance at meetings was eleven, which is very satisfactory.

During the year, eight General Meetings were held, at which the following papers were read :—

February 9th, 1926.—"Some Notes on the Search for Oil in France," by L. P. Timmins, B.Sc., F.G.S., M.Inst.P.T.

March 2nd, 1926.—"Modern Developments in Drilling Methods," by M. A. Ockenden, F.G.S., M.Inst.P.T.

March 16th, 1926.—"Petroleum Refining in Burma," by Maung-Ba-Yan, Stud.Inst P T.

October 21st, 1926.—Joint Meeting with the Geological Society. Short Address by Lieut. J. H. Blakiston, A.M.Inst.P.T., R.N.R.

November 6th, 1926.—"The Object of the Students' Section," by Prof. A. W. Nash, M.Sc., F.C.S., M.Inst.P.T.

November 23rd, 1926.—Joint Meeting with the Mining Society. "Recent Developments in the Design of Surveying Instruments," by W. H. Connell, Esq.

December 2nd, 1926.—Joint Meeting with the Geological Society. "The Use of the Eötvos Balance in the Field," by W. R. McDonald, M.I.Mech.E., M.Inst.P.T.

December 7th, 1926.—"Some Unsolved Refining Problems," by J. McConnell Sanders, F.I.C., F.C.S., M.Inst.P.T.

At the Annual General Meeting, which was held on May 19th, 1926, the following Officers were elected for 1926–27 :—

Chairman : Mr. G. T. Notley.

Vice-Chairman : Mr. H. V. Steadman.

Committee : Mr. M. A. Iaroslavici, Mr. R. G. Ffoulkes-Jones, one member to be elected next term (Mr. C. A. H. Williams was subsequently elected).

Hon. Secretary : Mr. L. P. Timmins, F.G.S.

The Institution's Scholarship for the year has been awarded to Mr. Guy Tunstall Notley.

The following Officers have been elected for 1927–28 :—

Chairman : Mr. R. G. Ffoulkes-Jones.

Committee : Messrs. G. Dickinson, C. A. H. Williams, T. B. C. Harris.

Hon. Secretary : Mr. L. P. Timmins, B.Sc., F.G.S.

(Signed) LAUNCELOT P. TIMMINS,
Hon. Secretary.

(Countersigned) T. H. HOLLAND,
President.

The President moved the adoption of the Balance Sheet, and in accordance with practice invited the Chairman of the Finance Committee to explain its leading features.

Mr. Alfred C. Adams: Once again it is my privilege to second the motion for the adoption of the Balance Sheet and to offer some explanatory observations on the accounts. I have had the honour of doing this for a good many years, and I am afraid that many of you will only hear to-night largely a repetition of what I have said before, because after all our accounts are presented in the same form year after year. It is a very good form, and its great advantage lies in its simplicity. You will see that the Balance Sheet indicates a very satisfactory financial position, a good deal of progress having been made during the year 1926. The Capital item on the liability side of the Balance Sheet has now been increased to over £2,000—£2,006 11s. an increase of £151 4s. On the opposite side of the account you will see the amount that has been invested—namely, £1,941 4s. 10d.—and the various securities in which that amount is invested are shown on the Balance Sheet. This item does not quite indicate the total of the capital, because we had about £65 in hand awaiting investment. That has since been invested. More money became available and £100 has since January 1st been invested, so that the Capital Account may now be said to be quite square. The Students' Prize and Scholarship Fund, the Research Fund account and the Students' Section Fund items all represent amounts which are in hand for the various purposes. The Research Fund appears on the opposite side among the assets, because the balance of the amount not expended in grants in aid for research work in 1926 was put on deposit, and there it remains. Indeed, we have already this year increased that amount by a further £400 in respect of the current year 1927; so that at the present moment, in accordance with the decision of the Council, there is an amount of about £767 devotable to research in the way that the Council has laid down. The Sundry Creditors represent items that occur at any accounting period. The largest item in the amount of £365 1s. is for the printing of the Journal, which was issued in December. On the other side of the account you will find amounts given for the Office and Library Furniture and the Library Books. Both of those items have been suitably depreciated so as to represent what we consider to be the value of the property. The item Sundry Debtors and Payments in Advance, £196 13s. 10d. represents various small amounts for advertisements in Journals and other small things which were all liquidated and cleared up in the early part of the year. You will notice that we have on deposit

the sum of £986 13s. 8d. and cash at bank and in hand of £221 9s. 6d. In addition to that we have a further sum of £501 19s. 6d., which is invested temporarily until the time comes when it has to be spent as the Council may decide. The net result of all this is that the Revenue Account has now a credit balance of £1,962 12s. 10d. As regards the Revenue Account, the items are fairly normal and do not seem to require very much comment; they follow very much the same course as in previous years. The cost of issuing the six Journals last year was £334 12s. 8d. This is a little less than the year before, but as you know, it represents the actual cost of printing the Journal after crediting the revenue derived from advertisements and the sales of the Journal. Subscriptions have now risen to the respectable sum of £3,052 14s. As the membership of the Institution continues to grow, the probabilities are that you will find, when next year's accounts are presented, that the revenue from subscriptions will have mounted still further in a gratifying manner. I think you will agree that the Balance Sheet before you shows that the Institution is in a thoroughly good position financially. I do not think I need take up any more of your time, and I will therefore conclude by seconding the motion made by the President from the chair: "That the Balance Sheet and Accounts for the year 1926 be adopted."

The resolution was then put and carried unanimously.

Appointment of Auditors.

On the motion of **Mr. C. Dabell**, seconded by **Mr. E. R. Redgrove**, Messrs. Price, Waterhouse & Co. were re-elected Auditors for the ensuing year.

Election of Council.

The Secretary announced that there were seven names on the ballot list, of which three were those of retiring members and four those of new nominations. As the result of the ballot, Mr. Ashley Carter, Mr. A. E. Chambers, Mr. A. Frank Dabell and Mr. E. H. Cunningham Craig were elected, of whom Mr. Ashley Carter, Mr. Chambers and Mr. Cunningham Craig were the retiring members.

Presentation of Student's Medal and Prize.

The President: I now have great pleasure, on behalf of the Council, in presenting to Mr. H. S. Garlick the Student's Medal and Prize awarded by the Council for his paper on "The Scottish Shale Oil Industry." This paper was one of eight submitted during the year that came within the qualifications laid down.

I am quite sure that the other Student Members will agree with me in congratulating Mr. Garlick on his success, because he has not only been a very active member of the Section and been full of public spirit in helping the Section, but, as you know, his paper last year received a special prize.

(The President then presented the Student's Medal and Prize to Mr. H. S. Garlick.)

The President: The Council also wish to announce that the papers in the students' competition were generally of high merit, but it was decided that we should limit our recognition by way of special mention to three papers only. The Committee of Selection recommended for special honourable mention the papers by M. Ba Yan on "Petroleum Refining in Burma," by Mr. W. B. Rountree on "Essential Qualities of Various Petroleum Products," and by Mr. J. O. Tanner on "Electrical Methods of Prospecting for Oil."

Induction of the President-Elect.

The President: I have now to perform what is to me the most pleasurable function of the evening and one in which I know the members will share that pleasue with me—namely, in asking you to receive your new President, Mr. Adams. Mr. Adams was one of the 29 Founder Members of the Institution. Since then he has been conspicuous as an active Member of Council, and he is well known to you for a series of most pleasant balance sheets—balance sheets that have been pleasant largely because of his careful financial nursing of the affairs of the Institution during each year. We have found him generous when some of us have wanted to devote money to new enterprises; at the same time we have realised that his generosity has only been accorded after due consideration of the merits of each proposition. We have thus received additional confidence in the proposals made when we knew that Mr. Adams was willing to finance them. I now have the very greatest pleasure in asking Mr. Adams to accept the Chair as President of the Institution.

(The Chair was then vacated by Sir Thomas Holland, and taken amid hearty cheering by Mr. Alfred C. Adams.)

The President (Mr. Alfred C. Adams): Sir Thomas Holland and Gentlemen, I have very warmly to acknowledge the great honour that the Council has conferred upon me in electing me as President of this Institution for the ensuing year. I recognise the very formidable task that lies before me when I think of the very high standard set by Sir Thomas Holland and the other Presidents who have preceded me in the Chair. But

having been called upon for nearly 50 years to devote my attention to problems connected with the petroleum industry, and it having been my lot to work for such a long time as a student of the general practical aspects of problems connected with petroleum, I am hoping that there will be no necessity for the Council to indulge in regrets for having elected me to the Chair. The Institution is rich in possessing a band of distinguished Past-Presidents who are able to devote, and do devote, a very great deal of time and care to the affairs of the Institution, both at the Council and outside. It is sometimes found in many Societies that the passing of the Chair synchronises with a certain slacking off of active interest, but nothing of the kind takes place in connection with the Past-Presidents of this Institution. They never flag in their energies; they are always anxious to do something more in the interests of the Institution, and I am quite sure that their advice and guidance will not be denied to me when it is needed. I recollect that two years ago our retiring President expressed the thought that in electing him the Council had discovered the smallest section of the three sections of which the Institution is composed, but I think we must say that he was wrong—he is not generally so. I think he overlooked one very small other section, because it appears that the Council has found a very minute section in the shape of what I may perhaps call, for want of a better term, the administrative section or the commercial section. It seems to me a little difficult, in an Institution which has been so often referred to as being tripartite in character, to account for the existence of a fourth section, however small it may be; but I think the most appropriate place for this inconspicuous section that I have the honour to represent in the triangular array of distinguished technologists of which the Institution is composed is at the point of the triangle where we know, on very good authority, it enjoys position, but no magnitude. At the same time, I hope this very small leaven will be productive of some good in helping the general team work of the Council. I think it is very necessary in an Institution like this that the Council should put in good team work, and I think the evidence that it does so is manifestly shown in many ways. It is evidenced in the accounts that you passed to-day, because I can assure you that, although I do something with regard to the accounts, after all, the Council has to scrutinise even what I do, and therefore the result is the production of the team work to which I have alluded.

Gentlemen, We have a lot of business to attend to to-night, but before a commencement is made with the papers that are to be read I desire to propose a very hearty vote of thanks to our retiring President, Sir Thomas Holland, for his magnificent work

in the conduct of the affairs of the Institution during the two years of his Presidency. There is no doubt that in him we have a man of tremendous energy and strength of purpose, and the benefit to the Institution of his wise guidance of their affairs has been an outstanding feature during the whole of the period of his Presidency. Although Sir Thomas is interested in and associated with many other scientific and technical societies in a similar way, I have always felt that he has shown a special interest in and a special pride in this Institution, and it is for that reason that it has been such a great pleasure to work under him during his Presidency. I have the very greatest pleasure in proposing that a very sincere vote of thanks be accorded to Sir Thomas Holland for his wise guidance of the Institution during the two years of his Presidency.

The resolution was carried by acclamation.

Sir Thomas Holland, K.C.S.I. (Past-President): Mr. President and Gentlemen, I thank you, Mr. President, very sincerely for the generous way in which you have made this proposal, and the members for the spontaneous manner in which they responded to your request. There is no doubt that the Institution has been to me a matter of special personal interest, because like yourself, Sir, I was one of the Founder Members. But for the war I should have been your President in 1916, having been elected by the Council in that year; but being ordered out of the country, like a good territorial, within a week after my election I had to give up the position. At any rate, the Institution did not suffer by my departure. There is one thing I can boast of which you, Sir, will never be able to boast of, and none of your successors either, and that is that I managed to get through the business of the Institution during the past year, which happened to be the 13th year in the history of the Institution, without any real disaster or trouble! With the help of my colleagues on the Council, whom I thank most sincerely for their cordial co-operation, and with the goodwill of the members of the Institution, we have managed to dupe the gods, at any rate this time, and I hope there never will be any danger to the Institution again from that source. I thank you, Sir, very much indeed for your kind remarks, and you, gentlemen, for the manner in which you received them.

The President: The next item on the Agenda is the placing before you of certain papers which have been prepared for the Second Empire Mining and Metallurgical Congress, which is to take place in Canada from August 22nd to September 28th next. From this point I should like to say that the meeting is private. No publication of anything that we do or say is

permissible, for quite obvious reasons, because these papers, although they will be read in abstract and a discussion will take place upon them, are not to be published in any way or dealt with in the Press until the date shown on the papers themselves—namely, August 22nd this year. I propose to ask Sir Thomas Holland to be good enough to explain to you the origin of this movement and the reason why these papers are brought before you to-night.

The following paper was then read in abstract :—

"Conditions affecting the Petroleum Prospects of the Engine," by Sir Thomas H. Holland, K.C.S.I., K.C.I.E., D.Sc., LL.D., F.R.S. (Past-President).

The President: I am sure you would wish me in your name to offer to Sir Thomas Holland our heartiest thanks for the very interesting abstract he has given us of his paper. There will be no opportunity this evening for any discussion of the papers that are to be read; the discussion will be postponed until an adjourned meeting, which will be held on Tuesday, April 5th, at 5 o'clock.

The following papers were then read in abstract :—

"Possible Auxiliary Sources of Liquid Fuels," by Prof. Alfred W. Nash, M.Sc., M.I.Mech.E., F.C.S. (Member).

"Economics of the Petroleum Situation in British Dominions," by Sir Frederick Black, K.C.B., B.A. (Past-President).

"Progress and Prospects of Production," by E. H. Cunningham-Craig, B.A., F.R.S.E., F.G.S. (Member).

"Petroleum Refining Facilities within the British Empire," by James McConnell Sanders, F.I.C., F.C.S. (Member).

The President: That concludes the business for this evening. I am sure you would like me to tell Sir Thomas Holland and the other gentlemen who have read papers in abstract that they have whetted our appetites very much by the interesting, condensed, tabloid form in which they have presented them.

The meeting then terminated.

"Pinking" in Internal Combustion Engines.

By G. B. Maxwell.*

"Pinking," which by its high-pitched metallic note warns the motorist that he is overrunning his engine, has been the subject of many papers since 1918. So far no general agreement has been reached as to the cause of the trouble, and it appears desirable to attempt a critical survey of the theories that have been advanced to account for it, and of the experimental work on which they are based.

Theories as to the Cause of Pinking.

The "Spontaneous Ignition" Theory.—Until recently little or no distinction was made between pinking and pre-ignition, though the marked difference in sound and in effect indicates that the two phenomena are not of the same nature. Ricardo[1] distinguished between the two and pointed out that the power and efficiency of the high-speed petrol engine were limited rather by the danger of pinking than by that of pre-ignition. Pinking, if serious, would, however, lead ultimately to pre-ignition. Ricardo attributed the "pink" to the sudden inflammation of residual unburnt charge owing to its compression by the expanding burnt and burning portion. The heat due to compression would be augmented by radiant and conducted heat; in this manner the ignition temperature of the unburnt residue was attained. At this point Ricardo considered that the unburnt gas inflamed almost instantaneously throughout its bulk and the rapid rise in pressure caused the cylinder walls to vibrate as though struck by a hammer. This may be styled the "spontaneous ignition" theory of pinking.

The same views were held by Tizard, who performed a series of experiments on the ignition by compression of mixtures with air of various fuels.[2] The apparatus, which was designed by Ricardo, need be described only briefly here. The mixtures were suddenly compressed in a cylinder of 4½ in. bore, the piston being held rigidly in position at the top of the stroke. The compression ratio was variable, and the pressure in the cylinder throughout the stroke and the occurrence or otherwise of ignition were recorded by a standard Hopkinson optical indicator. Later the work was

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* Reprinted by permission from "Fuel in Science and Practice," March, 1927, Vol. VI., No. 3.

[1] *Proc. N. E. Coast Inst. of Eng. and Ship.*, 1918, **34**, 316.

[2] *Ibid.*, 1921, **37**, 381.

extended, with improved apparatus, by Tizard and Pye.[3] In these later experiments a wider range of initial temperatures was possible, so that the necessary compressions were not so high. A modified Collins indicator, which gave a record on celluloid strip very suitable for enlargement, was employed.[4]

In those experiments in which the degree of compression was sufficient to ignite the mixture, the pressure records showed a lag period subsequent to the arrest of the piston, before the further rise in pressure due to inflammation occurred. It was found that this lag period, for a given mixture, decreased as the compression was raised; also that it varied for different fuels at the same mean temperature.

A comparison of the records for mixtures with air of heptane, ether and carbon bisulphide gave some interesting results. These fuels behave in a different manner in the internal-combustion engine, though they all gave low "self-ignition temperatures" when subjected to compression. The first two pink badly at low compression ratios in an engine, whereas carbon bisulphide was found by Ricardo to raise the permissible compression ratio in an engine using a given petrol to which it was added in increasing amounts. At first sight these differences in behaviour would appear to militate against the "spontaneous ignition" theory of pinking. Tizard and Pye, however, found that, in their experiments, carbon bisulphide gave much greater lag periods than did ether or heptane at the same temperatures. Accordingly, they suggested that the addition of carbon bisulphide to a petrol increased the lag period sufficiently to avoid spontaneous ignition of any portion of the cylinder charge before the normal combustion was complete.

Since the duration of the lag period must be a function of the temperature coefficient of the reaction velocity, it would appear that the tendency to pink is dependent on this coefficient, and also on the relation between the rate of heat addition to and heat loss from the unburnt charge.

For spontaneous ignition to occur, the unburnt charge must be compressed under conditions where heat loss will be a minimum and the rate of heat addition great. Thus the design of the combustion chamber, the condition of the internal surface, the nature and position of the source of ignition, and the thermal properties of the gaseous charge will all influence the danger and degree of pinking.

Ricardo and Tizard and Pye appear to be uncertain as to the subsequent order of events after "spontaneous ignition" of the

[3] *Phil. Mag.*, 1922, (VI.), **44**, 79; 1926, (VII.), **1**, 1094.
[4] *Ibid.* 1921, **37**, 381.

residual charge occurs in an engine cylinder. Tizard speaks of the setting up of detonation waves, though he is doubtful whether pinking and true detonation are the same. The term "detonation," however, is best reserved for a certain phase of gaseous combustion

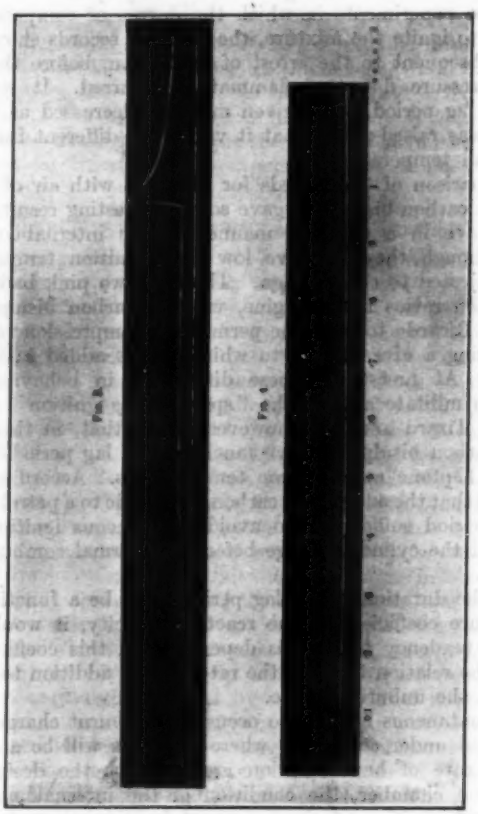

FIG. 1.

first observed by Berthelot[5] and, independently, by Le Chatelier.[6] When such an explosive mixture as electrolytic gas ($2H_2+O_2$) is ignited in a closed tube, the flame at first accelerates rapidly.

[5] *Compt. Rend.*, 1881, **93**, 18.
[6] *Ibid.*, **93**, 145.

If the tube be sufficiently long, after a period, which depends on the intensity and position of the source of ignition, a point is reached at which the mode of combustion suddenly changes. The flame now moves at a high and constant speed (about 2800

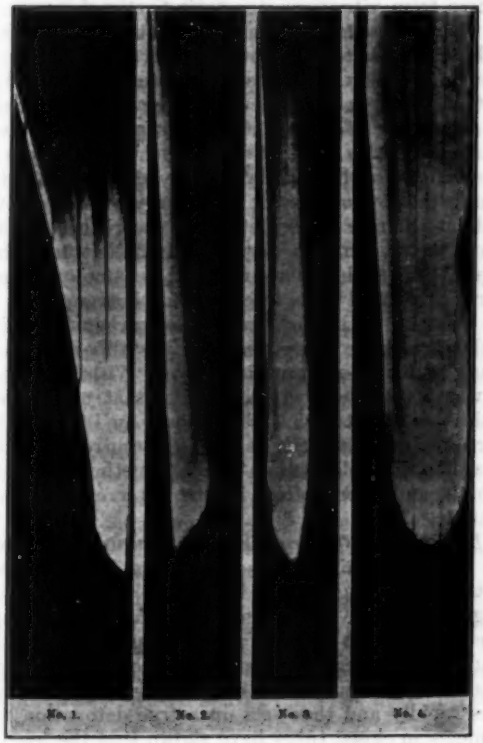

FIG. 2.

metres per sec. in electrolytic gas) and the flame front is marked by a narrow zone of very high pressure—the "detonation-wave."

An examination of the pressure records obtained by Tizard and Pye does not support the view that the inflammation of a gas when ignited by compression is of the same nature as in a detonating mixture. Fig. 1 shows two records obtained with the

Collins indicator for mixtures of air and hydrogen. The first slow rise in pressure marks the initial compression, which is followed by a lag period of considerable extent. Finally, ignition occurred in both cases, as shown by the further abrupt rise in pressure followed by the cooling curve. This second rise, though steep, is free from vibrations due to indicator shock such as are produced when a pressure-wave impinges on this form of manometer.

Similarly, in the photographs of flame in various mixtures ignited by sudden compression in a closed glass tube obtained by Dixon, Bradshaw and Campbell[7] the flame is seen to start from a point or layer, somewhat ill-defined, and takes an appreciable time to spread throughout the tube. Four of their photographs of flame in mixtures of carbon bisulphide and oxygen are shown in Fig. 2. In obtaining these photographs the films were moving vertically downwards at the rate of 20 metres per sec.; the tube was horizontal, and the piston was driven in from left to right of the photographs. Thus the more rapid the flame movement, the more nearly horizontal is its track in the photograph.

In no instance with such mixtures (carbon bisulphide and oxygen) did the flame travel through the tube with a velocity approaching that of the detonation wave. With the fastest flame the rate was 100 metres per sec., whilst that of the detonation wave in the same mixture has been shown by Dixon to be nearly 1800 metres per sec. Sometimes ignition occurred near the closed end of the tube as in photograph No. 1, sometimes near the piston as in No. 2, and more often in the intervening space as in Nos. 3 and 4.

The "Detonation" Theory.—From the considerations already advanced it appears fairly conclusive that a detonation wave will not be set up in an engine cylinder as a consequence of the spontaneous ignition of the residual unburnt charge. The use of the term "detonation" to express pinking has nevertheless become widespread amongst engineers, many of whom hold the view that, on ignition of the mixture in an engine cylinder, the flame at first accelerates rapidly and thus sets up a true detonation wave.

Experiments in closed tubes have shown that the length of preliminary run required (the acceleration period) is always greater, at ordinary temperatures and pressures, than is available in the cylinder of a petrol engine. Thus Dixon[8] found that the flame travelled 12 in. in electrolytic gas, initially at room temperature and atmospheric pressure, before the detonation-wave was initiated. In this case the spark-gap was 3 in. from the wall. If the gap were nearer to the end of the tube, the preliminary run was

[7] *Journ. Chem. Soc.*, 1914, **105**, 2027.
[8] *Proc. Roy. Soc.*, 1893, **53**, A, 451.

increased up to 4 ft., and in less explosive mixtures was even greater. The much more rapid acceleration presumed to occur in the engine cylinder is attributed to the high temperature and pressure, and to the marked degree of turbulence of the mixture. The activation of the unburnt charge by absorption of radiant energy and of electrons from the flame has also been suggested as a contributory cause.

The "Flame Vibration" Theory.—When an inflammable gaseous mixture is ignited at one end of a closed tube of considerable length photographs of the combustion show that the flame begins to vibrate when it has travelled some distance. These vibrations may or may not lead to the detonation-wave, depending on the nature of the mixture, but they frequently give rise to a high-pitched note which rather resembles the "pink" of an internal-combustion engine.

This similarity led J. D. Morgan[9] to suggest that the two phenomena were intimately connected. He examined the rate of flame propagation and the nature of the vibrations in mixtures with air of methane and of Birmingham coal-gas in tubes 12 and 24 in. long. His conclusions were that the vibrational motion depended on two factors: (1) The rate of heat generation in the flame front. This factor, together with the dimensions and form of the combustion space, will influence the flame speed; and (2) "appropriate vibration frequency" in the gas along the direction of motion of the flame. This is a function of the length of the column of gas. Since in an engine cylinder the point of ignition is fixed, only factor (1) can be held to operate, so that the vibrations will be most likely to occur when the most inflammable mixture is being employed.

The "Nuclear" Theory of Pinking.—Ricardo and other writers have generally assumed that, given a carburettor of normal design, any residual droplets of petrol would be completely evaporated before the charge in an internal-combustion engine was ignited. This evaporation would be aided by the rise in temperature during compression, and by contact with the hot cylinder walls and with the residual gases from the previous explosion. A consideration of the temperature-entropy diagrams for the more usual petrol engine fuels led Callendar, King and Sims[10] to conclude that such might by no means be the case. Unlike steam and alcohol, the saturated vapours of most fuels, at temperatures not exceeding their critical points, would condense, not superheat, when subjected to isentropic compression.

[9] *Journ. Soc. Automobile Eng.*, Jan. 8, 1925.
[10] *Engineering*, 1926, **121**, 475, 509, 542, 575.

In Fig. 3 is shown the temperature-entropy diagram for pentane. Starting with saturated pentane vapour at point B, adiabatic compression along line B D would lead to progressive condensation until only liquid is present at D. Thus in the case of hydrocarbon fuels, the complete evaporation of liquid nuclei in the induced charge would be retarded during compression, provided that

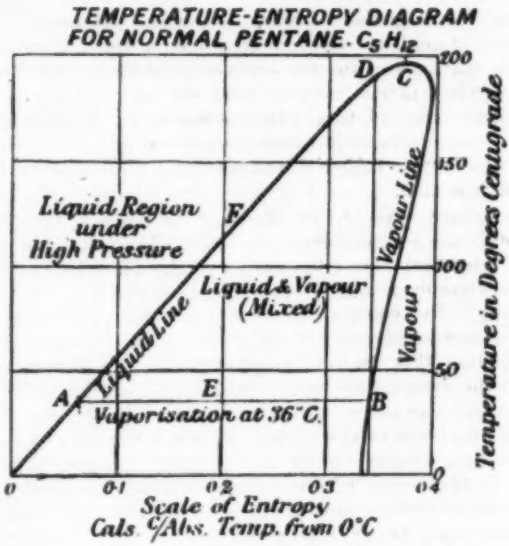

FIG. 3.

the critical temperature of the least volatile constituent were not exceeded.

Engler distillation tests of various petrols supported the view that high-boiling nuclei might be present at the moment of ignition in an engine cylinder. These would form a number of easily-ignitible points in the charge, since the paraffin constituents of petrol have progressively lower ignition temperatures as the molecular weight (and boiling point) increases. The surface of separation of a liquid and vapour is known to be highly reactive, whilst the formation and persistence of the nuclei would be aided by the presence of carbon particles, which might increase the reactivity by absorption of radiant energy.

In view of these facts, Callendar, King and Sims suggested that pinking is due to the simultaneous ignition of a comparatively

large volume of unburnt charge by the inflammable nuclei, with the production of a very sudden rise in pressure. The way in which this ignition is brought about has been the subject of further study by Callendar, but this work is described in detail later.

Factors Affecting Pinking in Internal-Combustion Engines.

Before a critical study of these theories is made a short consideration will be given to the factors which are known to affect the degree of pinking in an internal-combustion engine.

It is a matter of common knowledge that an engine is most liable to pink when it is running slowly under a heavy load at full throttle. The pinking becomes worse as the cylinder heats up and, if excessive and allowed to continue, will develop into pre-ignition. The change to pre-ignition is marked by a change in sound from a sharp clink to a dull thud, and by an immediate drop in power. At the compression ratios usually employed, slight pinking can be eliminated by retardation of the ignition, without apparent loss of power. However, pinking precludes that considerable gain in efficiency which could be obtained by the use of higher compression ratios.

Factors connected with Engine Design.—The most important of the factors affecting pinking which are connected with engine design is the compression ratio, that is the ratio of the total volume at the end of the suction stroke to the volume of the combustion space when the piston is at top dead centre. The operation of this factor is by no means clear, and is worth considering in some detail. In the first place, the effect of a higher compression-ratio cannot be attributed solely to the consequent increase in the temperature of the cylinder charge. Raising the ratio from 4 : 1 to 6 : 1 has very little influence on the calculated temperature on ignition (the ignition setting being the same at both ratios), since the temperature of the charge at the commencement of compression is considerably lower in the latter case. This lower temperature is due to the smaller proportion of hot residual gases mixed with the fresh charge. It is not certain, however, that calculations of gas temperatures during compression are applicable, owing to the lack of uniformity of the mixture in an engine cylinder and possibly to condensation of the fuel. In practice an increase in the compression ratio 4 : 1 to 6 : 1 would lead to violent pinking in most petrol engines. The ratio is usually limited to about 5 : 1.

Other factors connected with the design of the engine are the size of the cylinder, the shape of the combustion space and the position of the source of ignition. In order to avoid pinking it is generally held that the combustion space should be as compact

and as free from pockets as possible. Large cylinders lead to pinking at lower compressions than do small ones. Central ignition is the most suitable, but as this is not often practicable when poppet valves are used, the spark-plug should be opposite the inlet valve in order to keep the plug as cool as possible. This latter arrangement, however, is probably more efficacious against pre-ignition than against pinking.

Factors Connected with the Properties of the Fuel.

The factors affecting pinking which are not directly connected with the design of the engine include both chemical and physical properties of the fuel itself, and also certain other factors such as the fuel-air ratio, the charge density, and running speed.

Ricardo[11] has shown that the constituents of the common motor fuels may be arranged in the following order as regards their increasing liability to pink in a given engine—aromatic hydrocarbons (benzene, toluene, xylene), naphthenes, unsaturated hydrocarbons (ethylenic), paraffins. At one time the speed of flame propagation in mixtures with air of a given fuel was held to indicate directly its tendency to pink, but a comparison on the basis of flame speeds is not justified. For example, R. W. Fenning[12] found that the rate of flame propagation in a closed cylinder was greater in benzene-air than in hexane- or petrol-air mixtures.

These factors all involve a comparison of the behaviour of different fuels. When a particular fuel is considered, certain other variables are found to influence the degree of pinking.

As already stated, pinking is most marked at slow running speeds when the engine is labouring. This was attributed by Ricardo to the higher temperature and pressure attained in the cylinder at slow speeds. At high speeds, he suggested that there would be a greater proportion of inert residual gases in the charge owing to wire-drawing in the valves. It has been known for a considerable time that the trouble can be abated by dilution of the charge with inert gases which reduce the inflammation temperature and pressure. At first Ricardo considered that the greater turbulence of the mixture was responsible for the effect of increasing speed, but recent experiments have convinced him that the degree of turbulence has little or no influence.[13] It should be noted, however, that Tizard and Pye[14] found that a higher degree of compression was required to ignite a given mixture when turbulent in their apparatus. Again, throttling reduces the

[11] *Empire Motor Fuels Report*, 1923–24, Inst. of Automobile Eng.
[12] Aer. Res. Comm. Rep. No. 979, E. 15.
[13] "The Internal Combustion Engine," Vol. II. Blackie and Sons, 1923.
[14] *Loc. cit.*

trouble, apparently by reducing the volumetric efficiency and hence the charge density. This will decrease the explosion temperature owing to the greater dissociation of the products at the lower pressure attained. For the same reason the degree of pinking is very sensitive to altitude changes, and even to variations in barometric height from day to day.

The composition of the charge plays an important part. It is found that, for a given fuel at a certain compression ratio, pinking is most marked with the mixture which gives maximum power. This mixture, which for petrol or benzene is 10—20 per cent. rich, is the one in which the speed of flame and the explosion temperature and pressure are the greatest. It is probably due to slight variations in mixture strength that pinking only occurs spasmodically, even at fairly high compressions, and not for each compression stroke.

Factors Connected with the Addition of Inhibiting Agents to the Fuel.

A variety of substances are now known which, when added to the fuel, influence the degree of pinking at a given compression ratio. Of these the so-called "anti-knock" compounds will be considered first. These may be divided into three classes.

(1) *Organo-metallic Compounds*, such as lead tetraethyl, iron and nickel carbonyls. Extremely small quantities of these compounds have a surprising effect. Thus Callendar, King and Sims[15] state that less than $\frac{1}{4}$ fluid oz. of $PbEt_4$ per gallon of petrol raised the H.U.C.R.* 40 per cent. and increased the power 14 per cent. for the same fuel consumption. Such compounds are open to the objection that they give a metallic deposit in the cylinder which causes sticking of valves and contamination of the lubricant. The addition of an organic halide such as ethyl bromide to lead tetraethyl is said to eliminate much of the trouble with this compound.

(2) *Organic amines* such as aniline, toluidine and methyl aniline. These are required in quantities up to 10 per cent. by volume to be effective. They discolour the petrol and lead to the formation of tar, the sticking of valves and the fouling of plug points.

(3) *Aromatic hydrocarbons and naphthenes.*—These are not "anti-knock" compounds in the same sense as those in the first groups, but it is well known that a high aromatic content (usually benzene, toluene and xylene) in a petrol allows the use of higher compression ratios. Both naphthenes (saturated cyclic hydro-

[15] *Loc. cit.*

* Highest Useful Compression Ratio.

carbons) and unsaturated aliphatic hydrocarbons of the olefine class are less liable to pink than are the paraffins. Even the aromatic hydrocarbons, however, are far less effective, bulk for bulk, than either the organo-metallic compounds or the amines. About 50 per cent. of benzene is as effective as 5 per cent. of toluidine when added to a paraffin-base petrol. Ricardo found that the action of benzene or toluene in raising the H.U.C.R. with a given petrol was a straight dilution effect. It followed the mixture law, *i.e.*, the raising of the H.U.C.R. was directly proportional to the added amount of benzene or toluene. This relationship does not hold for the other two classes of "anti-knock" substances. Benzene is dearer than petrol, and supplies are at present limited, but so far the aromatic hydrocarbons are probably the most generally useful additions to petrol to prevent pinking since they do not lead to secondary troubles.

"*Knock-inducers.*"—Just as the three classes of compound described as "anti-knock" are able to limit the liability of an engine to pink, there are many substances, to which the name "knock inducers" has been applied, which have the opposite effect. Many of these are oxygenated compounds, for instance, amyl and butyl nitrites and organic peroxides, but others contain no oxygen in the molecule. As an example, bromine is said to act as a "knock-inducer," whereas iodine is a "knock-suppressor."

Discussion of the Theories of Pinking.

The "Detonation" Theory.—What has been styled the "detonation" theory of pinking is so widely accepted that it will be considered first. The view that a true detonation-wave is set up owing to the ignition by compression of the unburnt charge is plainly at variance with the experimental evidence. There still remains the possibility that the initial acceleration of the flame in an engine cylinder is so great that the detonation-wave is developed in certain instances. Experiments in closed vessels under similar conditions of temperature and pressure, with similar fuel-air mixtures to those in the engine, never show any evidence of flame speed and acceleration comparable with those obtaining in an inflaming mixture which is about to detonate.

It may still be argued that, with the highly turbulent state of the charge in an engine cylinder, the flame may be so accelerated that the detonation-wave is initiated after a very short preliminary period of normal combustion. Against this argument are the facts that pinking is most marked at low running speeds, and that Ricardo found the degree of turbulence to have little effect on the H.U.C.R. with a given petrol.

The high temperature and pressure in the mixture on ignition have similarly been adduced as factors leading to true detonation in the confined space in the cylinder. Dixon[16] certainly found that an increase in the initial pressure of electrolytic gas in a closed tube shortened the preliminary run before the detonation-wave was set up, and this observation was confirmed, for initial pressures up to 6·5 atms., by Dumanois and Laffitte.[17] On the other hand, Dixon[18] found that an increase in the initial temperature decreased the velocity of the detonation-wave in electrolytic gas, whilst Woodbury, Lewis and Canby[19] found that a high initial temperature delayed the initiation of detonation in acetylene-air mixtures enriched with oxygen. Their experiments were carried out in a closed cylinder, 12 in. long and 4 in. in diameter.

The Action of Anti-knock Compounds in the Light of the "Detonation" Theory.—To conform with the "detonation" theory, anti-knock compounds must either slow down the initial combustion or else modify the unburnt charge in the later stages so that the detonation-wave is not initiated. "Knock-inducers" must have the opposite effect.

With regard to these possibilities the following facts are known. The addition of lead tetraethyl does not affect the rate of inflammation (*i.e.*, of non-detonating combustion) of paraffin-air mixtures in closed vessels at normal initial temperatures and pressures. This fact makes it probable that lead tetraethyl will not have any influence on the length of preliminary run required before the detonation-wave is developed in a gaseous mixture initially at normal temperature and pressure. Dixon[20] has obtained experimental evidence which supports this inference.

There remains the possibility that the effect in an engine cylinder is due, not to the "anti-knock" compound itself, but to its decomposition products. Thus lead tetraethyl decomposes at a temperature of about 200° C. giving a fine cloud of metallic lead. The experiments of Egerton, however,[21] invalidate this view. Mixtures with air of pentane and acetylene were ignited at various initial pressures from 1 to 10 atms., and at initial temperatures of 23° C. and 230° C. The length of preliminary run before the detonation-wave was set up under these conditions was not appreciably altered by the addition of lead tetraethyl, though it is certain that this substance would be decomposed at the higher initial temperature.

[16] *Proc. Roy. Soc.*, 1892, **52**, A, 451.
[17] *Compt. Rend.*, 1926, **183**, 284.
[18] *Loc. cit.*
[19] *Journ. Soc. Automotive Eng.*, 1921, **8**, 209.
[20] Trans. Faraday Soc., Oct., 1926, p. 372.
[21] *Ibid.* p. 373; *Nature*, **119**, 259.

The inherent improbability of the initiation of a true detonation-wave within the confines of an engine cylinder, and the difficulty in explaining the action of "anti-knock" compounds, militate against the acceptance of the "detonation" theory. Indeed, it might be argued that endeavours to disprove the theory are a waste of time, since the term "detonation" is merely used loosely to express pinking, were it not for the fact that a considerable amount of work has been, and is still being, done on the assumption that the development of a true detonation-wave is the cause of the trouble.

Thus it has been suggested that the detonation-wave is a consequence of the activation of unburnt charge in the cylinder by radiant energy or by ionization due to electrons projected from the flame. Dopes, *i.e.*, "anti-knock" compounds, are assumed to act by absorbing either the radiant energy or the electrons. The first suggestion has resulted in papers by Clark and Thee[22]

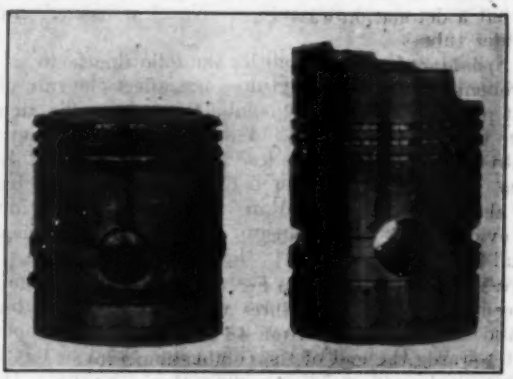

FIG. 4.

and by Henne and Clark[23] who investigated the effect of various dopes on the spectrum of a mixture exploding in an engine cylinder. They found that the spectrum of a pinking combustion showed an extension in the ultra-violet region. An "anti-knock" compound, by stopping the pinking, restored the normal spectrum.

The ionization suggestion has been a fruitful source of speculation, though so little is known of ions and of the phenomena that they induce. The effect of lead tetraethyl on the rate of decay of

[22] *Ind. Eng. Chem.*, 1926, **18**, 528.
[23] *Compt. Rend.*, 1927, **184**, 26.

ionization in a benzene-air mixture was examined by Wendt and Grimm[24] and by Clark, Brugmann, and Thee[25] who obtained contradictory results. Garner and Saunders[26] found that the electrical conductivity of an exploding hydrogen-oxygen mixture was depressed by "anti-knock" compounds and raised by "knock-inducers." This result and those of Clark and others on radiation, may be interpreted to mean that increased radiation and ionization are as likely to be the effects as the causes of pinking.

There is one practical application of the "detonation" theory that is of interest. This is the "stepped piston" described by Dumanois[27] which is shown in Fig. 4 alongside the original piston for which it was substituted. The effect of the steps is to deepen the combustion space progressively as the distance from the spark-plug is increased. Dumanois claims that the use of his invention raised the permissible compression ratio of a given engine from 4·6 : 1 to 6·7 : 1. This claim awaits confirmation. The idea was based on the work of Campbell[28] and of Laffitte[29] who showed that a detonation-wave was checked on sudden expansion into a wider tube.

The "Spontaneous Ignition" Theory.—A considerable amount of experimental evidence has been obtained in support of the view that pinking is caused by the sudden ignition of the unburnt charge in the engine cylinder. Thus, though Woodbury, Lewis and Canby[30] were unable to detonate ether-air mixtures in their apparatus, they frequently observed "auto-ignition" of the mixture ahead of the flame. In such cases they obtained photographic evidence of rapid vibrations in the burning mixture, and a loud knock was heard.

The pressure records shown in Fig. 5 were obtained by Fenning[31] on explosion of air-hexane mixtures at initial temperatures of 200-230° C. and initial pressures from 48·2-120·5 lb. per sq. in. It is seen that towards the end of the combustion, provided the initial temperature and pressure were sufficiently high, the manometer suddenly began to vibrate violently. The nature of the mixtures, the character of the experimental conditions and the slow rise of pressure during the early stages of the inflammation, do not indicate the possibility of detonation. An increase in the rate of burning owing to spontaneous ignition and probably the setting

[24] *Ind. Eng. Chem.*, 1924, **16**, 890.
[25] *Ibid.*, 1925, **17**, 1226.
[26] *Trans. Faraday Soc.*, Oct., 1926, p. 335.
[27] *Compt. Rend.*, 1926, **182**, 1378.
[28] *Journ. Chem. Soc.*, 1922, **121**, 2454.
[29] *Compt. Rend.*, 1924, **179**, 1396.
[30] *Loc. cit.*
[31] *Loc. cit.*

up of vibratory motion owing to the multiple flames would appear to be the most likely explanation of the disturbances. The effect was always accompanied by a loud knock.

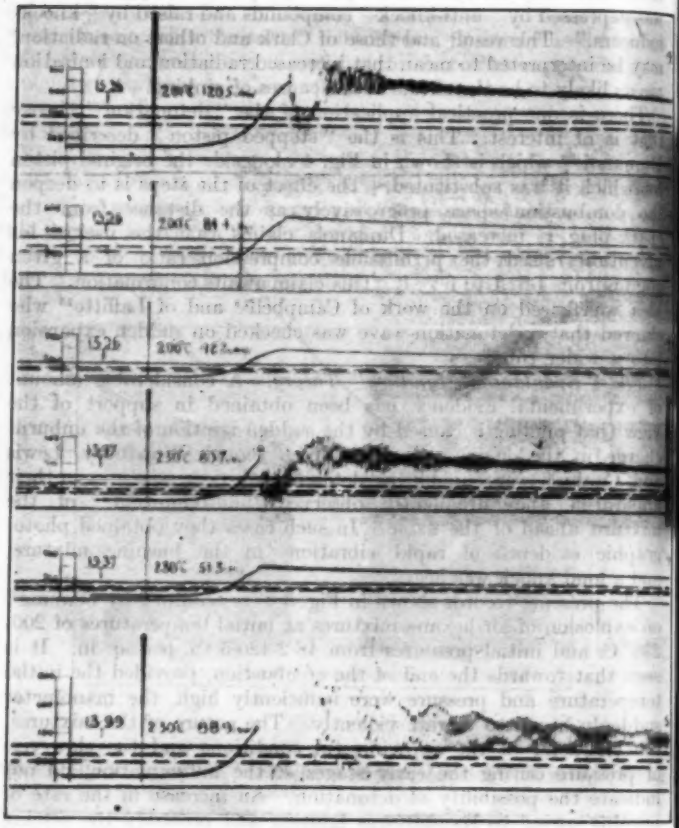

FIG. 5.

In connexion with these records of Fenning, it is interesting to find that a similar phenomenon had been noted by Petavel as early as 1902. Fig. 6 is a reproduction of one of his records.[22] The

[22] *Phil. Mag.*, 1902, **3**, 461.

manometer was of the well-known Petavel type and the record here reproduced was given by the explosion in a spherical vessel of a strong coal-gas-air mixture, initially under a pressure of 70 atms. About 0·05 sec. after the first rise the rate of pressure development suddenly increased to about 9 times its previous magnitude. Petavel calculated that the change occurred when the gas was at a mean temperature about equal to that at which it would ignite spontaneously.

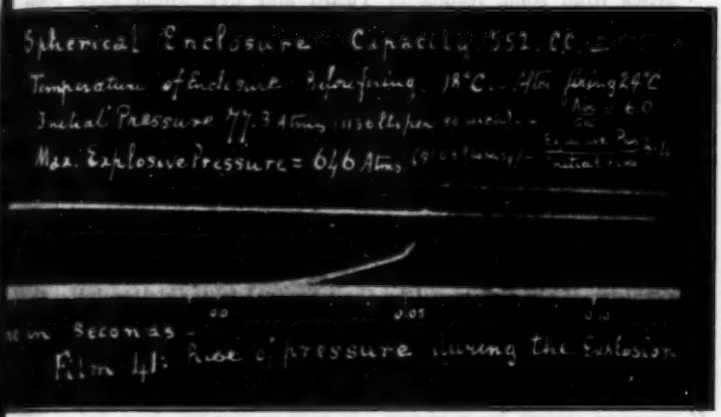
Spherical Enclosure Capacity 552 CC.
Temperature of Enclosure before firing 18°C. After firing 24°C
Initial Pressure 77.3 Atms
Max. Explosive Pressure = 646 Atms
0.00
0.05
0.10
Seconds
Film 41: Rise of pressure during the Explosion

FIG. 6.

Fenning came to the same conclusion from his experiments. From the observed pressure at the beginning of "knock," he calculated the mean temperature of the unburnt residue on the assumption that it was compressed adiabatically. The prevailing pressure at the moment of knock varied very greatly (the present records showed a range of 275-690 lb. per sq. in.), but the calculated temperatures of the compressed unburnt gas were nearly constant. This result gives support to the view that the effect was due to the spontaneous ignition of the unburnt charge.

When the behaviour of an engine in practice is considered, the "spontaneous ignition" theory accounts for most of the facts. Thus pinking occurs more readily in large cylinders than in small because the surface-to-volume ratio and therefore the cooling is less; more readily with paraffin than with aromatic hydrocarbons since the ignition-temperatures of the former are lower; more readily with paraffins of high molecular weight than with the lower paraffins for the same reason and also because

the flame temperature increases with the molecular weight. Lower charge densities, consequent on increased altitude or throttling, reduce the maximum flame temperatures and hence the radiant and conducted heat absorbed by the unburnt charge. Similarly other factors such as increased running speeds and dilution of the mixture which reduce the explosion temperature also tend to reduce the degree of pinking.

One of the objections to the "spontaneous ignition" theory arises from some results of Tizard and Pye which have been confirmed by Pignot.[33] These show that variations in mixture strength over a wide range appear to have but little effect on the ignition temperature as determined by the compression method. In an engine, however, the tendency to pink is always greatest with the mixture which develops maximum power.

This difficulty is probably more apparent than real. In the engine spontaneous ignition is held to be due to the compression and direct heating of unburnt gas by an advancing flame. When, as appears to be the case for the paraffin hydrocarbons, the ignition temperature and the temperature coefficient of the reaction velocity are almost independent of mixture strength, the temperature of the flame will be the principal factor determining the spontaneous ignition of the unburnt residue. This, as mentioned previously, is the greatest in the mixture which gives maximum power. In the compression apparatus the conditions are very different, since the ignition is due to the compression of a homogeneous system by a piston.

It is when the effect of dopes is considered that the most trouble is experienced in reconciling fact with theory.

Pignot[34] states that the addition of toluidine or diethyl sulphide to cyclohexane did not in any way affect the ignition temperatures on compression and Tyzard has confirmed this observation. Tanaka and Nagai[35] examined the effect of water and of various dopes on the spontaneous ignition temperatures in oxygen of a number of liquid fuels by the method of Moore.[36] It was found that the ignition temperatures of alcohols were considerably increased by the addition of small amounts of water or of organo-metallic or amine dopes, whereas those of hydrocarbons or of ethyl ether were little affected.

The "Nuclear Theory" of Pinking.—The action of dopes on the spontaneous ignition of the unburnt charge in an engine cylinder

[33] *Compt. Rend.*, 1926, **182**, 376.
[34] *Loc. cit.*
[35] *Proc. Imp. Acad. Japan*, 1926, **2**, 219–223.
[36] *J. Soc. Chem. Ind.*, 1917, **36**, 109; 1920, **39**, 36R.

and the accompanying very rapid rise in pressure are best explained by the "Nuclear Theory" of pinking.

It was found that an organo-metallic compound, to be effective as a dope, must decompose at a fairly low temperature (200–250° C.) with formation of a fine cloud of metallic particles. Indeed Mardles and Sims[37] showed that colloidal suspensions in petrol of iron, nickel and lead had the same "anti-knock" properties as the same weight of metal in the combined form (*i.e.*, as ethide or carbonyl). The nuclear theory assumes that the fine metallic particles will deposit on any liquid or solid surfaces in the cylinder, particularly if such surfaces possess a slight radius of curvature. If the metallic deposit decreases the tendency of the nuclei to ignite, then the effect of such minute amounts of organo-metallic dopes is understandable.

The action of the organic amines in suppressing pinking is very satisfactorily explained by the nuclear theory. A comparison of the "anti-knock" values of different amines with their critical temperatures, boiling and ignition-points, shows a close connexion between the two classes of property. For a given ignition temperature (which is much higher for the aromatic amines than for the paraffin constituents of petrol), the "anti-knock" value increases with the boiling-point and critical temperature. The action can thus be attributed to the concentration of the amine in the nuclear drops, whose tendency to ignite will thus be increased.

Against the nuclear theory it can be argued that it applies to saturated vapours, whilst the fuel-air mixtures used in practice are so far from saturation that the formation of liquid drops is very doubtful. However, the Engler distillation tests of various petrols by Callendar showed that some high-boiling fractions are always present, and that these may either be carried over into the cylinder in the form of a mist or spray, or else brought to saturation point and condensed on compression. Any electrification generated by friction in the induced charge would favour the persistence of the nuclei. The fact that most volatile No. 1 petrols pink more readily than the heavier commercial grades, which would be expected to condense more readily, may be due to the presence in the latter of greater amounts of impurities such as sulphur compounds. These are known to have a certain "anti-knock" value.

A more serious objection to the theory was the explanation of the action of organo-metallic dopes, but this has to a great extent been overcome by the recent work of Callendar[38]

[37] *Engineering*, 1926, **121**, 605.
[38] *Ibid.*, 1927, **123**, 147, 182, 210.

The fine metallic clouds produced on thermal decomposition of those organo-metallic compounds which have "anti-knock" properties oxidise very readily in air, with rapid evolution of heat. It would appear that they would tend rather to act as multiple ignition points than to retard the ignition of the nuclear drops. When an examination was made of the chemical changes undergone by various fuel-air mixtures during preliminary heating before ignition occurred, several interesting discoveries were made. Pinking fuels were found to oxidise at much lower temperatures than non-pinking fuels, and the products of this incipient oxidation were found to contain traces of highly oxygenated compounds, believed to be organic peroxides, particularly if the fuel were passed through a combustion tube in the form of a spray. Organic peroxides are usually unstable, explosive compounds, and are frequently decomposed by fine metallic particles. If such peroxides are formed in the engine cylinder—and evidence was obtained in favour of this view—then the action of dopes becomes much clearer. The preliminary oxidation of the paraffins was found to proceed most readily in very rich mixtures, so that the action would be most marked near the surface of the nuclear drops where the fuel concentration is high. When a dope has been added, however, the metallic deposit on the nuclear drops will tend to decompose peroxides as fast as they are formed. Callendar's experiments showed that the addition of suitable metallic compounds and of amines inhibited the formation of peroxides.

The "Flame Vibration" Theory of Pinking. Morgan's theory of "flame vibration" is inadequate to explain the underlying causes of pinking, but it quite possibly applies to the most noticeable effect, namely the metallic clink through which the trouble is first made apparent. It is a well-known fact that flame-vibrations in a closed tube give rise to a similar note, and it has also been shown that the spontaneous ignition of unburnt gas in a mixture which is partly inflamed gives rise to such vibrations.

Conclusions and Suggestions for Future Research Work.

From this critical survey it is evident that further experimental evidence is required on certain points. The spontaneous ignition theory, as modified by Callendar's nuclear hypothesis, seems to fit the facts better than any other suggestion put forward. A more detailed examination of the oxygenated compounds formed during preliminary oxidation of paraffin hydrocarbons is required, since the formation of organic peroxides has not yet been definitely proved. The solution of titanous sulphate used to detect their presence is said by Engler[39] to be a test for hydrogen peroxide, not

[39] *Ber.*, 1898, **31**, 3046.

for organic peroxides. The latter, however, form hydrogen peroxide in presence of moisture by antoxidation, so that they react to titanous sulphate if not carefully purified. It would appear that the action of "knock inducers" on peroxide formation must also be investigated.

As a preliminary to engine experiments, the mode of combustion of fuel mists in a closed cylinder, at various initial temperatures and pressures, would repay photographic examination. The effect of preliminary "baking," and of a variety of "anti-knock" substances and "knock inducers" could in this way be determined.

If these and similar experiments confirm the nuclear theory of pinking, then there will be two main lines of attack on the problem of eliminating the trouble. In the first place there is the question of finding a really satisfactory "anti-knock" compound, which will inhibit peroxide formation without causing secondary troubles. This side of the problem is intimately connected with the chemical examination of liquid fuels with a view to removing any impurities which catalyse the preliminary oxidation. On the engineering side it would appear likely that certain modifications or improvements in refining practice would repay attention. It is conceivable that if any small amount of entangled high-boiling liquid passes through the dephlegmators with the petrol vapour it is a possible cause of pinking in the internal-combustion engine. In this connexion the possible effect of electrification of the induced charge on the formation and persistence of fuel mists must also be considered.

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I. The Effect of Metallic Vapours on the Ignition of Substances.

By A. EGERTON, F.R.S., and S. F. GATES, B.Sc., M.A.*

1. GENERAL INTRODUCTION.

CONSIDERABLE interest has been raised by the discovery of the effect of very small quantities of lead tetraethyl and other substances in allaying the "knock" which occurs with some fuels under certain conditions in an internal-combustion engine (Midgley).[1] Both practical and theoretical reasons have evoked this interest. There is need, both for a satisfactory "antiknock" and for clarity as to their mode of action. These investigations, mainly made on behalf of the Asiatic Petroleum Company, have thrown some light on the latter point. We are indebted to the company for permission (given on February 1) to publish the account of the work which follows. We are also very grateful for the permission to mention some of the results of the work carried out by Messrs. Ricardo and Co. with the variable compression engine in conjunction with our own experiments on igniting temperatures. Also we wish to point out that Dr. R. A. Weerman, of the Laboratory of De Bataafsche Petroleum Maatschappij in Amsterdam, first drew attention to the effect on igniting temperatures which we describe, and which we have followed up.† We are grateful to him, and to Messrs. Kewley, Marshall and Jenkin, of the technical staff of the Company, for their collaboration.

Part of this investigation published in the Proceedings of the Royal Society[2] related to the determination of the detonating properties of various mixtures of acetylene and pentane. It was there established that for mixtures that could be detonated in a tube 150 cms. long "antiknocks" did not affect the position of detonation, even up to initial temperatures of 230° C., and pressures of about 100 lbs. per sq. in.

The investigations branched in many directions; the three papers which follow *summarise* the work, which dealt with:—

(I) The effect of metallic vapours on the ignition of substances.
(II) The significance of igniting temperatures.
(III) The effect of certain organic compounds on the igniting and "knocking" characteristics of petrol.

* Paper received April 11th, 1927.

† See this *Journal* pp. 300–307.

[1] Midgley (and co-workers). *J. Soc. Aut. Eng.*, 1922, **10**, 7, 218, 374, 451 *et seq.* *J. Soc. Eng. Chem.*, 1922, **14**, 589, 849, 894, *et seq.*

[2] Egerton and Gates. *Proc. Roy. Soc.*, 1927, **114**, 137.

A fourth paper reviews the above work and discusses the reasons for the effects observed. It develops views of processes of combustion and ignition, and supplies a theory of antiknock action.

The work was carried out between February, 1925, and May, 1926. A full report of the experimental work and an outline of the theory of antiknock action put forward was made to the Asiatic Petroleum Company in June, 1926, and was lent to the Air Ministry in October, 1926. A summary by the Secretary was laid before the Aeronautical Research Committee in December, and considered by them in January simultaneously with the Reports of the Air Ministry Laboratory (vide *Engineering*, February, 1927).[3]

2. It is not intended in this first paper to discuss either practical or theoretical possibilities, but to set on record a series of experiments which rapidly limited the field of search for antiknocks and also limited the possibilities as to their mode of action.

At the outset of the work it was known that antiknocks (such as lead tetraethyl) had little effect on the adiabatic ignition point of a combustible mixture, and that the igniting temperature of petrol as carried out in a Moore apparatus was practically unchanged by their addition (Ormandy and Craven).[4] This fact, though correct was shown to be misleading. Dr. R. A. Weerman found that a large rise of the igniting temperature of petrol occurred if the test were carried out in a particular way in a current of air instead of oxygen. It was established by numerous parallel experiments in engines with many different substances that the same chemical action must be responsible for the rise of igniting temperature as for the "antiknocking" tendency, see p. 250, and Part II., p. 270. The present paper deals with the effect of certain metallic vapours on the igniting temperature of petrol, and several other combustible substances.

3. The first experiments were designed to show whether lead, lead oxide or the organo-metallic compound itself is responsible for the rise in igniting temperature of petrol.

(*a*) It is unnecessary to describe the apparatus in detail. The principle is much the same as that described by Moore[5] and others. A drop of combustible liquid is allowed to fall through a small hole in the lid into an iron pot uniformly heated. A measured current of air is led into the pot through a copper tube inserted near the base. The temperature of the interior of the pot is measured by a thermocouple. The temperature at which the vapours suddenly ignite is recorded. 0·25 per cent. of lead tetraethyl in petrol (Shell) caused 160° C. rise in the igniting temperature of a drop of a certain

[3] Callendar. *Engineering*, 1927, **123**, 147, 182, 210.
[4] Ormandy and Craven. *Journ. Inst. Petr. Techn.*, 1924, **10**, 335.
[5] Moore. *J. Soc. Chem. Ind.*, 1917, **36**, 109.

size (0·0125 c.c.), which was allowed to fall into the ignition chamber. If instead of adding the lead ethyl to the petrol prior to introduction, it was permitted to enter as vapour with the air into the pot, a rise of over 145° C. was obtained. (The temperature of the U-tube containing the lead ethyl was adjusted to give about the same concentration of lead ethyl in the vessel.) This experiment proved two points: the effect of the lead ethyl was much the same whether introduced as liquid or as vapour, and secondly the effect of the vapour was not impaired by the air, before burning occurred in the heated chamber.

(*b*) Next, the air supply was passed through a bulb in the centre of which were mounted two lead electrodes between which a high-tension spark was maintained. Lead oxide (PbO) was produced as a fine dust and carried into the ignition chamber along with the air. Only a small rise of igniting temperature occurred, varying from nothing to twenty degrees. Instead of using air, argon was passed through the spark bulb and mixed with the air stream at the point where it entered the copper tube leading to the ignition chamber; although the ignition point of the petrol was raised by the presence of the excess of argon, there was no difference when the spark was on or off. A low-tension arc was next substituted for the spark, and the argon stream was not allowed to meet the air except in the ignition chamber itself so as to avoid preliminary oxidation of the lead, a rise of igniting temperature of about 60° C. occurred when the arc was burning.

(*c*) These experiments were continued under conditions more comparable to those of the experiments with petrol to which lead ethyl had been added, so that a better comparison of the effect of metallic lead from the arc and the lead from the ethyl compounds could be made. Nitrogen was passed from a cylinder through a flow-meter into a tube fitted with an arrangement for maintaining the arc, consisting of a graphite crucible which holds the molten metal and an adjustable electrode of carbon or of iron. Oxygen was added through another flow-meter so as to enrich the air supply in oxygen to make up for the additional nitrogen passing in with the lead and to bring the composition of the gas stream entering the pot to that of air. A rise of 70° C. was observed when the arc was on. Determinations of quantity of metal carried into the chamber with the nitrogen were made by passing the gas through a small weighed quartz tube containing quartz wool, first without the arc on so as to ensure constancy of weight, and then with the arc on. In the above experiment 0·2 mg. of lead entered the chamber per minute along with 860 c.c. of air (at the temperature of the chamber). On the other hand, using petrol containing 0·25 per cent. lead ethyl the quantity of metallic lead in one drop was 0·02 mg. The volume

of petrol vapour from the drop was about 5 c.c. at the temperature in question. The concentration of lead in the chamber (70 c.c.) would therefore be about 0·2 mg. in 650 c.c. of air. The rise in ignition point in this particular experiment was 95° C., so that for much the same quantity of lead the rise is of the same order in the two cases. It was reasonable to conclude, from such experiments, that the effect of lead ethyl in raising ignition point was due *primarily* to metallic lead formed in its decomposition. It is necessary to say "primarily," as it is probably the oxidisability of the lead so formed that is the essential feature.

TABLE I.

I Effective	II. Ineffective	III. Doubtful Results With Arc.	IV. Not Tested: Probably Effective.	V. Difficult to Test by the Method.	VI. Not Tested: Probably Ineffective.
Thallium	Aluminium	Iron*	Lithium	Titanium*	
Potassium	Magnesium	Nickel*	Caesium	Zirconium	Silicon*
Lead	Mercury	Tin*	Rubidium	Thorium*	Boron*
(Iron)	Iodine	Cerium*	Barium	Scandium	Beryllium
(Nickel)	Phosphorus	Vanadium*	Strontium	Tantalum	Germanium
Manganese	Gold		Gallium	Tungsten*	Arsenic*
Bismuth			Indium	Niobium	
Selenium				Molybdenum	
Tellurium				Chromium*	
Sodium				Cobalt*	
Cadmium				Platinum metals*	
				Uranium*	
Calcium					
Antimony					
(Copper) v. slight					
(Zinc) v. slight					
(Silver) v. slight					

* Tested by other methods.

4. These methods were applied to test the effect of other metals. Table 1. shows in column 1 elements which have been found effective, more or less in order of effectiveness. In column 2 are found those which are ineffective. In column 3 those which have given doubtful results by the method. In column 4 those which, likely enough, would also be effective. In column 5 those which, owing to their low volatility, could not be satisfactorily tested by the method. In column 6 those which similarly could not be tested, but which probably would not be effective. The rise obtained in the case of thallium was nearly 200° C. It was particularly interesting that potassium and sodium were effective. The sodium, potassium, selenium, iodine and phosphorus were introduced by passing the nitrogen or argon over the surface of the metal heated to a definite temperature (the vapour pressure of the metal determines the upper limit of the concentration of the metal entering the combustion chamber). Table II. summarises the experiments.

TABLE II.

Expt.	Element.	Conditions.	Igniting Temperatures. Without Arc.	With Arc.	Rise.	Mgms. per min.
			°C.	°C.	°C	
1	Cadmium	Iron Cathode in N_2, molten metal anode	460	510	50	—
9	„		460	500	40	0·25
2	Carbon Arc.		450	447	(–3)	—
3	Bismuth	Iron Cathode in N_2, molten metal anode	450	520	70	—
13	„	„ „	460	550	90	0·7
4	Aluminium	„ „	435	440	(5)	—
5	Iron	„ „	460	480	20	Very little
6	Antimony	„ „	455	475	20	0·3
7	Mercury	„ „	480	490	10	0·74
8	Tin	„ „	(500)	500	—	0·3
10	Zinc	„ „	485	490	5	0·66
11	Copper	„ „	470	475	5	(0·04)
12	Nickel	„ „	460	470	10	0·06
14	Lead	„ „	460	560	100	0·2
15	Thallium	„ „	465	>650	>185	0·3
17	Gold	Carbon-Gold in A	470	470	—	traces
18	Potassium	Tube at 400°C in A	435	500	65	<0·4
		Tube at 500°C in A	445	505	60	<1·6
19	Sodium	Tube at 520°C in A	450	450	—	Nil.
		Tube at 670°C in A	450	515	65	<5·2
21	Magnesium	Iron-Mg. in A	470	475	(5)	—
22	Cerium	Carbon-Cerium in A	470	475	(5)	Very little
23	Calcium	Calcium-Calcium in A	470	500	30	0·22
24	Manganese	Carbon-Manganese in A	470	540	70	0·10
25	Copper	Copper-Carbon in A	445	475	30	0·30
26	Selenium	Heated tube in A	450	490	40	<0·4
27	Iodine	„ „	455	440	—15	5·0–0·2
28	Lead	Carbon-lead in A	455	570	115	0·4
29	Lead	Carbon-Lead in N_2	460	555	95	0·55
30	Thallium	Carbon-Thallium in A	465	620–645	180	0·04
31	Iron	Iron-Iron in A	465	475	10	trace
32	Zinc	Heated tube (600°C) in A	462	464	—	—

Expt.	Element.	Conditions.	Igniting Temperatures. Without Arc. °C	With Arc. °C	Rise. °C	Mgms. per min.
33	Zinc	Zinc-carbon arc in A	470	490	<20	>0·7
35	Silver	Silver-carbon in A	460	475	15	0·1
36	Phosphorus	Heated tube at 125°C in A	470	460	—10	—
37	Vanadium	Carbon-Vanadium in A	460	460	0	traces

A few comments on these experiments are necessary. A change of igniting temperature less than 10° C. can be ignored. There was decidedly no effect in the case of aluminium, mercury and magnesium; metal was definitely entering the igniting chamber in all these cases. On the other hand, the effect of cadmium, bismuth, manganese and calcium and also antimony was definite. It was difficult to vaporise sufficient iron, nickel, silver or copper, but these metals seemed to have only a slight effect; it was definite that appreciable though small amounts were carried into the igniting chamber. Judging from the effect of nickel and iron carbonyl on the igniting temperature, it seems probable that such metal as is carried into the chamber from the arc is not in a suitable form to act as an antiknock. The metal is formed at too high a temperature to be effective, that formed from carbonyl being in a more active condition. Using comparatively large currents it was probable that some particles of cerium and vanadium were produced, but the amount was small and the effect negligible. Gold has definitely no effect; its presence at the mouth of the tube within the igniting chamber was ascertained. The effect of potassium did not increase on raising the vapour pressure, probably because only a small fraction is uncondensed before entering the chamber. If the extra oxygen was added to the argon stream just after leaving a tube containing sodium instead of being added to the air stream, then very little rise was obtained (less than 10° C.); therefore it appeared that if the sodium was oxidised to a stable oxide it had no effect. In fact, the sodium carbonate deposited on the iron surface of the igniting chamber acted as a catalyst to ignition, the igniting temperature was lowered 80° C., and could not be recovered till the surfaces were washed free of alkali. Iodine similarly affected the surface of the igniting chamber. Metal (e.g., lead) deposited on the surface of the base of the chamber, did not affect the igniting temperature. In the experiment with selenium, little entered the chamber, but by heating the inlet tube the igniting temperature was raised 90° C. There appeared to be a slight positive effect when the concentration of zinc vapour was very high: but the effect of

this metal is exceedingly slight; the same applies in the case of tin. In all experiments, the effect of the metal is similar to the effect of the organo-metallic derivatives where they are available for comparison, except for those differences (Fe, Ni, etc.) already noted.

As a result of this work, it may be stated that:—

(1) Only oxidisable metals influence the igniting temperature.
(2) The metal itself in a state of incipient oxidation is the effective influence.
(3) Metals forming peroxides are usually effective.
(4) The most effective metals are molten and vaporisable at the igniting temperatures (except Fe, Ni, etc.).

Experiments were carried out on a variable compression engine, with the assistance of Messrs. Ricardo and Co. at Shoreham, to correlate the above results with engine behaviour.

Lead vapour distilled from an arc in a stream of nitrogen and passed into the engine cylinder produced a rise in H.U.C., whereas a carbon arc gave no such effect. It appeared, however, that the effect was quite as great when air was used in place of nitrogen; it is probable that the lead was produced in a more finely-divided state than in the experiment described on p. 246, and although oxidised was effective. A thallium arc was also found effective.

5. The behaviour of the metal vapours in the arc experiments is similar to the effect, on the igniting temperatures of petrol, of the many different organo-metallic derivatives which have been tested by Dr. Weerman or the present authors. Amongst those may be mentioned the following:—

Substance (Concn. 0·1% Vol).	Rise of Igniting Temperature. °C.
Selenium diethyl	140
Iron carbonyl	130
Bismuth triethyl	120
Lead ethyl	90
Nickel carbonyl	40
Tellurium diethyl	55
(Tin tetraethyl	50)
Bismuth triphenyl	42

The results are in general agreement with the effect of these substances on "knocking" in engines. Bismuth triethyl in the engine was ineffective owing to its instability and rapid decomposition. Tin tetraethyl and certain other compounds (diethylselenide) were less effective in the engine, no doubt owing to a difference in the condition of temperature and pressure, to which they are exposed. Mercury and zinc diethyl, aluminium and boron triethyl were definitely ineffective, both in the pot and in the engine. In the case of elements which cannot be readily vaporised, it has been possible in many cases to test their effectiveness by making an

organo-metallic derivative. The advantage of the method we have described lies in the fact that the element itself is utilised so that, as in a case like potassium, its behaviour can be studied although the derivatives may be too unstable to be used.

Various other investigators [1], [6], [7], [8] have compared the effect of metallic derivatives in engines, and the following conclusions may be drawn :—

(1) Aryl compounds are, as a rule, more stable and less effective than alkyl.
(2) Compounds in which the metal is directly attached to oxygen are as a rule ineffective.
(3) Only oxidisable metals are effective (e.g., platinum and gold compounds are ineffective).
(4) The effect of a compound depends on the proportion of metal atoms which on dissociation would be free and uncombined; for instance, lead triethylchloride is stated[7] to be three-fourths and diethyldichloride one-half as effective as lead tetraethyl.

Sims and Mardles,[8] using metal-organosols, have investigated the behaviour of various metals on engine "knock." Their results also pointed to the dispersed metal atom as the seat of the effect. The method is confined to those metals which give suitable organosols. These data afford additional support to the conclusions arrived at as a result of our experiments with the arc.

TABLE III.

Substance	Igniting Temperature.	Rise with $PbEt_4$.	Substance	Igniting Temperature.	Rise with $PbEt_4$.
Benzene	(690)	18	Pentane (2)	540	87
Cyclohexane	535	27	Amylalcohol	490	nil.
Methylcyclohexane	470	92	Amylenehydrate	640	35
Pentane (1)	515	75	Valeric aldehyde	320	390
Isohexane	525	46	Dimethylaniline	445	nil.
Heptane	430	83	Carbon disulphide	120	nil.
Petrol (Shell)	460	82		Igniting Temperature	Rise with $Ni(CO)_4$
Ether	440	65			
Alcohol	515	(0)	Cyclohexane	535	18
Acetaldehyde (Iron vessel)	395	110	Petrol	450	45
(Silica Vessel)	350	170	Carbon bisulphide	120	nil.

[6] Callendar, King and Sims. *Engineering*, April 9th, 1926, *et seq.*
[7] Church, Mack and Boord. *Ind. Eng. Chem.*, 1926, **18**, 534.
[8] Sims and Mardles. *Trans. Faraday Soc.*, 1926, **22**, 363.

6. The effect of lead tetraethyl on the igniting temperature of some other vapours has been investigated. Table III. summarises these results. 0·25 per cent. by vol. of lead ethyl is added to the fuel in each case (except in the case of amylene hydrate, when 0·5 per cent. was added). Points of particular interest are:—

(1) The self-igniting temperatures of normal alcohols are little affected.
(2) Those of aldehydes are very greatly raised.
(3) The igniting temperature of methylcyclohexane is more affected than that of cyclohexane.
(4) The effect on benzene which has a high igniting temperature is only slight.
(5) The effect on the igniting temperature of isohexane is less than on that of normal hexane.

Nickel carbonyl acts in a similar manner to lead tetraethyl, though to a less extent. The effect on the series pentane,* valeric aldehyde, amylene hydrate and amyl alcohol is specially instructive. A few experiments have been made on the igniting temperatures of gases (see Part II., p. 260) puffed into the ignition chamber (Table IV.). The effect on the igniting temperature of hydrogen was only

TABLE IV.

	Ignition Temperature.	Rise with $PbEt_4$.
H_2	680	15
"	"	17
CO	775	nil
CH_4	800	(5)
C_2H_2	370	25
C_5H_{12} vapour	670	35

slight, and whether there was an effect or not was not definite. There appeared to be no effect whatever on the igniting temperatures of carbon monoxide or of methane, but that on acetylene and on pentane vapour was definite. It may be mentioned here that Tanaka and Nagai[9] found that lead ethyl has a negligible effect on the igniting temperatures of hydrocarbons. A current of oxygen and a Moore ignition apparatus was used. The igniting temperatures are much lower under such circumstances (petrol 270° C.—300° C.). The result is not surprising, and is in agreement with that of Ormandy and Craven[4] and our observations. Tanaka and Nagai found indeed a slight effect on the igniting temperatures of ethyl alcohol, but the igniting temperature of alcohol in oxygen is considerably higher (350-400° C.). (See Part II., p. 258 and Table II.).

* The second value for pentane refers to a purer sample kindly supplied by Professor S. Young, F.R.S.

[9] Tanaka and Nagai. *Proc. Imp. Acad. Tokio*, 1926, **2**, 221.

7. There is a further observation which may be mentioned here. It provides information as to the question, "what happens when antiknocks are hindering the ignition of a combustible vapour?"

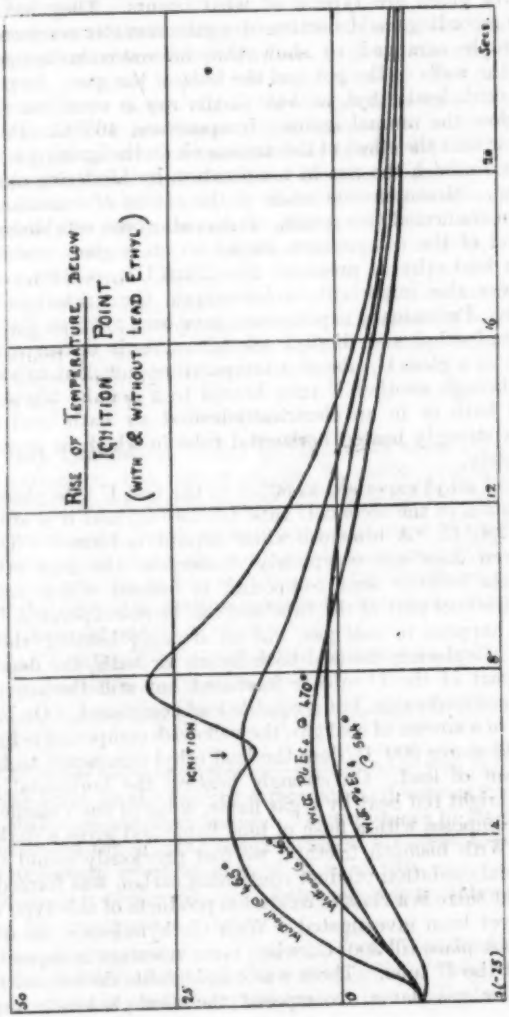


FIG. 1.

If the temperature of the vapour in the ignition chamber is observed below the "igniting point," after addition of a drop of combustible, the rise of temperature is not so great when the antiknock is present. The curves given are typical of what occurs. They have been found by recording the deflection of a galvanometer connected to a thermocouple arranged to show the difference in temperature between the walls of the pot and the bulk of the gas. In presence of 1 per cent. lead ethyl, at 544° C. the rise is even less than at 10° C. below the normal igniting temperature, 465° C. It is perfectly clear that the effect of the antiknock on the igniting temperature is to diminish the rise in temperature by hindering oxidation of the fuel. Measurements made of the extent of oxidation prior to ignition confirmed this result. It has also been established that at the end of the compression stroke on an engine, oxidation is less when lead ethyl is present. (See Part III., p. 278).

8. It was also important to investigate the oxidation of the antiknock. Preliminary experiments have been made on the oxidation of lead ethyl and diethyl selenide. Air is drawn over the antiknock in a glass U tube at a temperature sufficient to vaporise it, then through another U tube heated to a definite temperature in a lard bath or in an electrically-heated air bath, and finally through a strongly heated horizontal tube in which to decompose it completely.

With lead ethyl vaporised at 50° C. in the first U tube there is no decomposition in the second U tube till 230° C., and it is still very slight at 280° C. A brownish-white deposit is formed. The gas burner even does not completely decompose the lead ethyl, a yellow-white volatile lead compound is formed which sublimes easily on the cool part of the tube and can be re-evaporated. Much the same happens in coal gas, but on strongly heating, the solid blackens. Replacing the lard bath by an air bath, the deposit in the cool part of the U tube is increased but still the compound formed is not lead oxide, but a volatile lead compound. On heating to 400° C. in a stream of coal gas, the yellowish compound is formed, and not till above 500° C. does the lead ethyl commence to form a grey deposit of lead. On strongly heating the horizontal pyrex tube to a bright red heat by a gas flame, some of the volatile compound decomposes with a flash of blue flame and gives a dark grey deposit. With bismuth triethyl, we had previously found that a white partial oxidation product containing carbon was formed, and it is evident there is a class of oxidation products of this type which have not yet been investigated. With diethylselenide, no decomposition took place till 300° C., when some selenium is deposited at the exit of the U tube. There was considerable decomposition at 360° C. The gas flame decomposed the diethylselenide vapours

in the horizontal tube depositing selenium. At a red heat, the diethylselenide vapour catches fire and no doubt forms SeO_2. Nickel carbonyl in the same apparatus was found to decompose at 100° C. to metallic nickel.

It seems generally believed that lead ethyl dissociates into metallic lead and hydrocarbons which, in fact, it does, when heated in a sealed tube or when heated strongly locally. But the above experiments throw a new light on the peculiar oxidation which normally occurs on heating in air and are quite contrary to the notion that pyrophoric lead particles are formed (see Ref.).[7]

Callendar and Sims and Mardles[6],[8] have investigated the thermal decomposition of lead ethyl and nickel and iron carbonyls. Our experiments are really not at variance with their observations, which were made under different conditions, namely, at much higher concentration. It is noted that at 0·5 c.c. per 100 c.c. concentration, lead ethyl in petroleum jelly did not commence to blacken till 290° C.; it seems probable also that the white fumes they observed in presence of air were of similar nature to the product obtained in the experiments here described.

Summary.

It is only intended to record in this paper these observations. Their bearing on the nature of the catalytic processes, which determine antiknock action will be dealt with in the last paper.

(1) "Antiknocks," such as lead tetraethyl, raise the self-igniting temperature of certain combustible vapours. (This observation was made for the first time by Dr. R. Weerman in 1925 in the laboratory of the Bataafsche Petroleum Maatschappij in Amsterdam.)

(2) Lead volatilised or dispersed by means of an arc in nitrogen or argon has a comparable effect.

(3) The same method has been applied to test the effect of other metals.

(4) The metal atom in incipient oxidation is the seat of the action.

(5) The effect on the igniting temperature of various combustible substances has been tested. There appears to be very little effect on the igniting temperature of an alcohol, but a very pronounced effect on that of an aldehyde.

(6) The effect of the presence of the metal is to delay oxidation of the combustible substance.

(7) The decomposition and oxidation of "antiknocks" have been investigated, and the existence of a class of volatile intermediate oxidation products has been indicated.

II. The Significance of Igniting Temperatures.

By A. Egerton, F.R.S., and S. F. Gates, B.Sc., M.A.*

The object of this Paper is firstly to record the experiments which have been made on the conditions affecting igniting temperatures, and secondly to discuss the significance of such temperatures. It forms a study which has been essential to the development of the ideas put forward in the last Paper of this series, but does *not* contain any reference to the behaviour of anti-knocks.

1.—Ignition Points and Igniting Temperatures.

When a combustible mixture is heated, the rate of oxidation increases until there comes a moment when the rate of gain of heat by a volume element of the vapour balances the rate of loss of heat. The "ignition point" of that volume element of the mixture is the temperature at which this balance is reached. If the temperature is exceeded, the reaction rapidly accelerates until the products are raised to a temperature such that an appreciable amount of energy is emitted in the visible regions of the spectrum: the vapour is then said to "inflame."

Dixon and others [1] photographed mixtures undergoing adiabatic compression. He showed that the temperature calculated from the adiabatic rise of pressure could rise several hundred degress above the ignition point before luminosity appeared. Diffuse luminosity first occurs in a small region of the gas, not throughout the whole volume. The investigations of Tizard and Pye [2] have shown that the temperature coefficient of the reaction determines the duration of the delay before ignition for given conditions of loss of heat to the walls. Knowing the rate of loss of heat and the extent of the delay, it is possible to find the average temperature at which ignition occurs from the adiabatic compression temperature. The results agree for cylinders of different size and shape and confirm the definition of an "ignition point." The definition implies that if there were no loss of heat, and the conditions therefore truly adiabatic—

* Paper received April 11, 1927.

[1] Dixon, Bradshaw and Campbell, *J. Chem. Soc.*, 1914, **105**, 2027. Dixon and Crofts, *J. Chem. Soc.*, 1914, **105**, 2036.

[2] Tizard and Pye, *Phil. Mag.*, 1922, **44** (VI.), 79.

ignition would occur immediately, and inflammation as soon as the velocity of reaction had sufficiently accelerated.

Other methods have been used for determination of ignition points. In the concentric jet method (Dixon and Coward [3]), the reacting gases are preheated and then allowed to mix in a chamber uniformly heated to the same temperature. The temperature at which inflammation occurs is determined at various rates of flow. As far as possible, errors due to rate of mixing, to surface action and loss of heat to the surroundings are avoided, but these cannot be avoided completely. The ignition point for hydrogen and air determined by Tizard and Pye was 410° C., the concentric jet method (Dixon) gave 630°. The figures obtained by Tizard and Pye for various fuels, using the adiabatic method, are as follows :—

TABLE I.

	°C.		°C.
Pentane	316	Ether	227
Hexane	307	Carbon bisulphide ..	226
Heptane	298	Cyclohexane	324
Octane	297	Benzene	370

Many determinations have been made of the temperature at which vapours inflame by dropping the corresponding liquids into a heated chamber. But the influences of surface and of mixture, which affect the concentric tube method, are still more to the fore. It is preferable to call such temperatures " igniting temperatures " ; sometimes they have been termed " self-ignition temperatures." In Moore's [4] apparatus, a drop of the liquid is allowed to fall into a heated platinum crucible ; a preheated current of air or oxygen is led into the crucible. Holm [5] employed a porcelain tube. Tausz and Schulte's [6] apparatus was similar to Moore's. Some of the results obtained are given in Table II, together with the present authors' results. There is general agreement, but as might be expected the igniting temperatures for a given substance differ according as to whether oxygen or air is used, and according to the size, shape and material of the igniting chamber.

2.—The Determination of Igniting Temperatures.

The apparatus for the determination of igniting temperatures was similar in most respects to that which has been used by

[3] Dixon and Coward, *J. Chem. Soc.*, 1909, **95**, 514.
[4] Moore, *J. Soc. Chem. Ind.*, 1917, **36**, 109.
[5] Holm, *Z. angew. Chem.*, 1913, 273.
[6] Tausz and Schulte, *Mitt. Chem. Tech. Soc. Karlsruhe*, 1924, 2.

Dr. Weermann. A drop of liquid (about 0·012 c.c.) falls from a burette into an iron pot of dimensions 1½ in. diameter by 2¼ ins. high. Through the side of the pot near the bottom, a copper tube leads in a stream of heated air at a rate of 330 c.c. per minute. The temperature within the pot is measured by a thermo-couple placed near the plate forming the bottom of the pot. The pot is placed within a second thicker iron vessel which is heated electrically. The mass of the iron vessel and the adequate lagging assist in

TABLE II.

Igniting temperatures.

Substance.	M.	H.	T.S.	E.G.	T.N.	Substance.	M.	S.	T.S.	E.G.	T.N.
Benzene	566	520	740	700		Ethyl-alcohol	518	510	558	515	
			662		*513*		*395*		*425*		*340*
Xylene	484	500		780		Acetone		570	700		
									588		*504*
Toluene	516		810	780		Acetaldehyde		380	185	395*	
			552						*140*		
Cyclohexane				535		Benzaldehyde			188		
					318				*180*		
Methyl-cyclohexane				470		Carbon bisulphide				120	
					312						
Pentane (1)				515		Aniline		530	770	750	
									530		
Pentane (2)				540		Xylidine				820	
Hexane			487			Dimethyl-aniline				440	
			268		*322*						
Isohexane				525		Benzonitrile				625	
Heptane				430		Phenol			715	730	
					285				*574*	500	
Decane			463			Thymol					
			202								
Ethyl-ether	347	400	343	440		Kerosene (380)			293	320	
			178		*200*				*270*		*267*
						"Petrol"	383				
							272				

* Probably contained paraldehyde and acetic acid.

Note.—Oxygen figures in italics.

maintaining a uniform temperature. The temperature at which the vapour will ignite on letting in a drop of the liquid when the pot is being heated and that at which it ceases to ignite on allowing the pot to cool, are observed. They agree as a rule to ± 5°. The pot is kept clean and polished inside.*

* A thin film of oxide forms and protects the metal from further oxidation unless the temperature is high (> 650°) or substances such as halogens are present in the fuels when oxidation proceeds rapidly.

Results will be found for various liquids in the fourth column of Table II. It may be noted:—

Xylene	inflames at a higher temperature than		benzene.
Aniline	"	"	xylidine.
Lower paraffins	inflame	"	higher paraffins.
Cyclo-hexane	inflames	"	Methylcyclohexane.
Benzene	"		Cyclohexane
Phenol	"	"	Thymol.

Table III indicates that an alcohol possesses a higher igniting temperature than the corresponding hydrocarbon, but that the corresponding aldehyde has a much lower igniting temperature.

TABLE III.

Igniting temperatures of liquids.

Substance.	A.E. and S.F.G. with air.	T. and N. with oxygen.	T. and S. with air with θ_2.
Pentane	515	—	—
Amylalcohol	490	*364*	409 *390*
Amelene hydrate	840	—	—
Valeric aldehyde	320	—	—
Valeric acid	690	—	—
n-Propylalcohol	555	*328*	505 *445*
Isopropylalcohol	700	—	590 *512*
n-Butylalcohol	—	*334*	450 *385*
Ethyl alcohol	515	*340*	558 *425*
Acetaldehyde	395	—	185 *140*
Petrol	450	—	—

The more open the chain the lower the igniting temperature, as shown by the results for the various amyl and propyl alcohols.

Table IV gives figures for certain gases obtained in the same apparatus. A puff of gas is allowed to pass into the apparatus through a narrow capillary tube inserted through the tube which leads in the air supply. The volume puffed in was arranged to be about equivalent to the amount of combustible let in as a drop when the liquids were used. The temperature at which explosion or ignition occurred was independent of the volume of the gas entering, within fairly wide limits: the igniting temperature seemed to be sharply defined within ten degrees. Under such cir-

cumstances, hydrogen ignites violently with a sharp explosion and delay of one second after closing the inlet tap (c.f. p. 264). Carbon monoxide ignites with a quiet flash but a slight bluish flame is visible within the pot 20° below the igniting temperature (c.f. Dixon and Coward).[3] Methane ignites quietly with an almost invisible flame, and acetylene with a loud "pop" and much flame (c.f. p. 264). No flame was visible in the pot before ignition except in the case of CO, neither was any rise of temperature shown by the thermo-couple due to flameless combustion prior to ignition comparable to the rise occasioned by petrol and other substances below

TABLE IV.

Igniting temperatures of gases.

Substance.	Igniting temperature. ° C.	Ignition point concentric tube method (Dixon).
Hydrogen	680* ..	630
Carbon monoxide	775 ..	(850)
Methane	800 ..	748
Acetylene	370 ..	(428)

* Moore[7] obtained for hydrogen and air 686° and for hydrogen and oxygen 678°.

their igniting temperatures. It will be noticed (see Table IV) that the igniting temperatures are not very different from the ignition points quoted by Dixon, Harwood and Higgins[8] for ignition after a lag of about half a second. (Those in brackets are determined by his former apparatus and method, and are lower than would be the case for ignition after half a second interval.)

3. OBSERVATIONS ON CONDITIONS AFFECTING IGNITING TEMPERATURES.

The determination of an igniting temperature, it must be agreed, is a very empirical matter; the actual values depend on many conditions connected with the particular apparatus used. It is ven surprising that the values obtained do not show greater disagreement. It is with a view to investigating the importance of the various conditions that the following observations have been made:

(*a*) *Behaviour of an evaporating drop.*—When a drop of liquid enters the furnace, it falls on the polished base plate and separates into smaller droplets, which assume the spheroidal state. It takes 2–3 seconds for the drops to evaporate. If the temperature is high enough, ignition occurs after an interval of about 3 seconds

[7] Moore, *Journ. Inst. Petr. Techn.*, 1920, **6**, 200.
[8] Dixon, Harwood and Higgins, *Trans. Faraday Soc.*, 1926, **22**, 267.

from the moment of entry of the drop. If the surface of the plate, on the other hand, is considerably oxidised, the drop seems to shatter at once and the spheroidal state is not formed. Under these circumstances, ignition still occurs 2–3 seconds after entry, though for petrol the igniting temperature is about 100° lower.* The layer of iron oxide can be readily scraped off and even if the scrapings are left in the pot, the ignition point rises to the normal value. A halide (CCl_4, $C_2H_2Br_4$, etc.) seems immediately to induce this type of oxidation and to lower the igniting temperature, the pot having to be thoroughly cleaned before being used again.

(*b*) *Change of Quantity.*—If the size of the drop is increased or two drops are let in, the igniting temperature may be decreased, but not by more than about 10°. Doubling the air supply does not increase the temperature more than about 10°. The size of the air inlet tube, the dimensions of the ignition chamber, the size of the hole in the lid and the temperature of the lid all affect the igniting temperature to varying extents. The presence of two small iron plates (1½ by 1cm.) hung in the pot from the lid was found to raise the igniting temperature of petrol as much as 60°.

(*c*) *Effect of Surface.*—The material of the walls of the pot influence to some extent the igniting temperatures, but not to as great an extent as might be expected. Oxidation of the surface of the metal (particularly in the case of copper) has, however, a considerable influence. The following results were obtained with silica pots of the same size as the iron pot and with discs of various metals placed on the base of the silica pot :—

Igniting temperature of	Iron Pot.	Silica Pot I.	Silica Pot II. Alone.	Iron disc.	Platinum disc.	Copper disc.
Petrol	450°	470°	450°	445°	460°	420°
Acetaldehyde ..	395°	350°	—	—	—	—
Valeraldehyde .	320°	—	320°	—	—	—
Pentane ..	515°	505°	—	—	—	—
Alcohol ..	515°	—	505°	—	—	—

Surface action is very marked in some cases. Acetone does not ignite in the silica pot at 750°, while in the iron pot no ignition occurred even above this temperature. There is, however, a large amount of flameless surface combustion at much lower temperatures, as shown by the rise in temperature on letting in the drop. A rise of 130° was obtained at 500° in the case of acetone but attended by no visible flame or audible ignition. The rise is less at 700°. In the silica pot the rise is less than in the iron pot. For most substances the rise is not nearly so great and does not commence till

* In the neighbourhood of the igniting temperature, when oxygen is used instead of air, the delay before ignition may be 5 to 10 seconds.

about 75° below the igniting temperature. The position of the couple has some influence on the amount of the rise observed; but a few figures indicating the amounts are given in Table V. The rise is very marked for phenol, propyl alcohol and for acetone but particularly slight for aldehydes.

TABLE V.

Substance.	Rise 10° C. below I.T.	Substance.	Rise 10° C. below I.T.
Xylene	40	*n*-Propylalcohol	100
Toluene	25	Isopropylalcohol	55
Cyclohexane	10	Valeric acid	30
Petrol	25	Amylene hydrate	25
Isohexane	5	Amyl alcohol	35
Heptane	20	Valeric aldehyde	<5
Kerosene	10	Pentane	10
Acetone	70	Phenol	90
Alcohol (ethyl)	15	Aniline	50
Aldehyde (acet.)	<10	Xylidine	80
Ether	<10	Dimethylaniline	10
Carbon bisulphide	nil	Methane	<5
Hydrogen	<10	Acetylene	25
Carbon monoxide	< 5		

The graph obtained for a drop of petrol in the manner described in Part I, p. 254, shows the increase in temperature of the vapour over that of the walls at a position 7–8 mms. away from the wall. There is first a momentary fall due to evaporation of the drop, then a rapid rise. The temperature often rises higher than the igniting temperature without ignition occurring. The temperature rise observed is sometimes less just below the igniting temperature than at a somewhat lower temperature; one reason may be that the rate of loss of heat is greater the higher the temperature, another that the nature of the reactions change (see Part IV, p. 284). Fatty acids and aldehydes could be detected in the products of combustion below the igniting temperatures.

Other experiments have been made by introducing glass wool into the pot round the sides, thereby increasing the surface (and to some extent decreasing the volume). The effect was to raise the igniting temperature very materially, as the following figures show:

	Silica pot.	Ditto—glass wool.
Petrol	405°	550°
Acetaldehyde*	225°	>700°
Alcohol (abs.)	480°	525°

The results show that the extent of the surface is more important than its nature. These results are further discussed on p. 267.

* The igniting temperature of acetaldehyde varies very considerably according to purity.

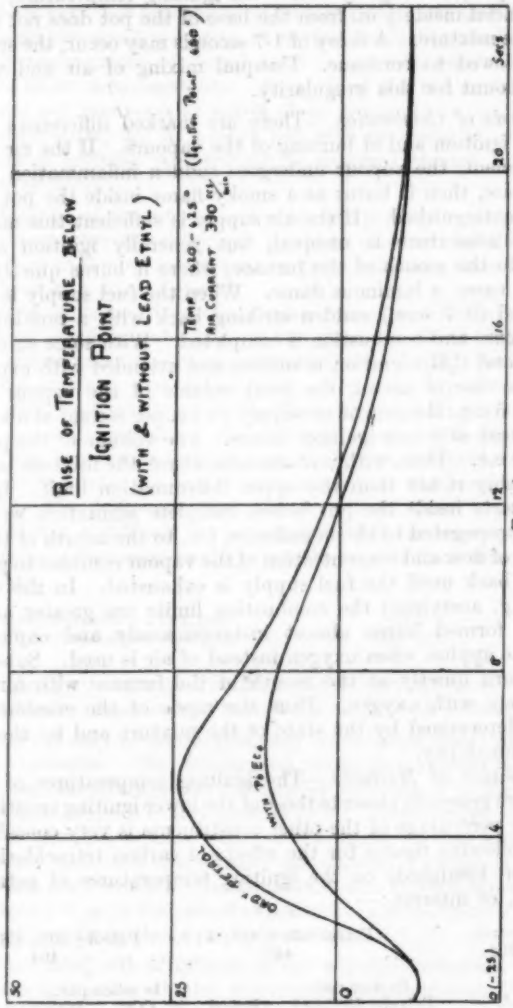

RISE OF TEMPERATURE BELOW IGNITION POINT
(WITH & WITHOUT LEAD ETHYL)
TEMP 610 - 615°
AIR CURRENT 330 c.c. per min.
(IGNITION POINT 680°)
SECS
20
16
12
8
4
0
25
0
50
OBD² PETROL
WITH Pb Et₄

FIG. 1.

(*d*) *Effect of Spark Ignition.*—After letting a drop into the pot at a temperature slightly below the igniting temperature, a $\frac{1}{8}$-in. spark placed inside $\frac{1}{2}$ in. from the base of the pot does not always ignite the mixture. A delay of 1-7 seconds may occur, the sparking being allowed to continue. Unequal mixing of air and vapour must account for this irregularity.

(*e*) *Mode of Combustion.*—There are marked differences in the mode of ignition and of burning of the vapours. If the air supply is insufficient, the vapour undergoes sudden inflammation with a slight noise, then it burns as a smoky flame inside the pot and is quickly extinguished. If the air supply is sufficient this may still occur if admixture is unequal, but generally ignition spreads rapidly to the mouth of the furnace, where it burns quietly with, in many cases, a luminous flame. When the fuel supply is nearly exhausted (5–7 secs.) sudden striking back with a non-luminous flame occurs and combustion is completed. With some substances (e.g. H_2 and C_2H_2) ignition is sudden and attended with explosion.

In the case of petrol, the total volume of the vapour would be about 5 c.c., the rate of air supply 15 c.c. per second at about the temperature at which ignition occurs. The volume of the pot was about 70 c.c. Thus, with uniform admixture, the mixture becomes considerably richer than the upper inflammation limit. Ignition which starts inside the pot before complete admixture would be rapidly propagated to the boundaries, i.e., to the mouth of the pot. The rate of flow and concentration of the vapour combine to prevent striking back until the fuel supply is exhausted. In the case of gases (e.g. acetylene) the combustion limits are greater and the mixture formed burns almost instantaneously and explosively. The same applies when oxygen instead of air is used. Substances which burn quietly at the mouth of the furnace with air, burn explosively with oxygen. Thus the mode of the combustion is mainly determined by the state of the mixture and by the limits of inflammability.

(*f*) *Ignition of Mixtures.*—The igniting temperatures of mixed liquids are generally closer to those of the lower igniting constituents, until the percentage of the other constituents is very considerable.

The following figures for the effects of carbon tetrachloride and of carbon bisulphide on the igniting temperatures of petrol are, however, of interest:—

Petrol.		Petrol + 20% CS_2 4 : 1.		Petrol + 50% CS_2 1 : 1.
394	..	445	..	494

	In iron pot.		In silica pot.	
Petrol.	Petrol + 10% CCl_4	Petrol + 5% CCl_4.	Petrol + 1% CCl_4.	
445 ..	— ..	335° ..	440°	
430 ..	325° ..	— ..	—	

Carbon bisulphide raises the igniting temperature of petrol in spite of its own very low igniting temperature (see p. 271 and Table II). A remarkably small quantity of carbon tetrachloride lowers the igniting temperature of petrol both in an iron and a silica pot in spite of its inflammability. In an iron pot the surface of the iron does not recover and petrol alone continues to ignite at the low temperature, but in a silica pot with no metal at all present the normal igniting temperature is regained though apparently not immediately.

(*g*) *Ignition of vapour and of liquid.*—Experiments were made to ascertain whether any difference would be observed for the ignition of a vapour in the pot introduced as vapour and the same substance introduced as a drop of liquid.

Pentane contained in a closed glass vessel was heated to 50° C. The short capillary tube beyond the glass tap fitted through the side of the furnace into the copper tube through which the air is fed. The tube and tap were kept warm. The quantity of vapour let in was varied without appreciable effect on the igniting temperature. In the second experiment, the delivery tube—a fine bore copper tube— was arranged round the base of the pot, the pentane vapour was delivered into the centre undoubtedly at the temperature of the pot. The following were the results of these experiments, from which it is difficult not to conclude that the vapour from the liquid drop ignites more readily than the vapour itself under similar conditions.

	I.	II.
Igniting temperature of liquid	515° ..	520°
Igniting temperature of vapour	655–690° ..	685°

The rate of mixing with the air cannot be very different in the two cases. Similar experiments have been made with hexane.

Ignition, it may be noted, generally occurs soon after the droplets became invisible. The evaporated molecules possess a greater energy than the average and this applies particularly to the smallest drops which evaporate at a greater rate. Furthermore, oxidation no doubt proceeds at the surface of the liquid, so that some of the evaporated molecules are already peroxidised. Hence conditions for ignition are favoured. Inflammation once started would spread more rapidly if, as in the case of vapour form a drop, there is a steady supply of vapour in the immediate vicinity.

(*h*) *Ionisation.*—It is difficult to say whether ionisation precedes and causes ignition or whether it is merely attendant to and favoured by the rise in temperature due to ignition. The presence of a few extra ions (as provided by β-rays from 3 mgs radium bromide or from passage of air through an arc) was found to make no difference

to the igniting temperatures of fuels. Experiments showed that there were at the igniting temperature many ions of thermal origin present in the mixture in the pot, but whether ionisation is concomitant to or an essential part of the combustion process is not yet clear. The evidence for the latter view is conflicting (see Garner and Saunders[9], also Finch[10]). Garner and Saunders give a summary of the work that has been done on this subject.

4.—The Significance of Igniting Temperatures.

It will be unnecessary to discuss each of the above observations as they can mostly be explained in accordance with certain general considerations about ignition.

(*a*) *Discussion of Conditions affecting Igniting Temperatures.*—If a uniform gas mixture is enclosed in a vessel which is at a uniform temperature above the "ignition temperature" of that mixture then presumably the gas ought to ignite. Nevertheless, in the determination of "igniting temperatures," the walls of the pot and the mixture itself may be considerably above the ignition point, as determined by the adiabatic method, without ignition occurring. It has to be remembered that an ignition point is defined as that temperature at which the average rate of heat loss balances the rate of gain of heat from the reaction. In the adiabatic method, it is to the average temperatures of the whole of the gas that the ignition point is normally referred, but small regions of the gas may possess much higher temperatures. Ignition starts in one or more of these centres* where the intrinsic energy of certain molecules is high and where the rate of heat loss cannot keep pace with the heat available from the increase in rate of reaction. Adiabatic ignition, of course, necessitates ignition under conditions of high pressure.

In the "pot" method of igniting vapours, heat is only picked up from the walls and the inlet pipes, and the rate of supply depends on the conductivity of the walls and on convection. Average temperature may be higher than is necessary for ignition by adiabatic compression, but convection of heat may be sufficiently great to prevent ignition, which must primarily be set up in centres of high energy content. Diffusion is paramount. Tizard and Pye's[11] experiments on the effect of turbulence indeed illustrate the importance of the dissipation of heat, in raising the ignition point determined adiabatically. For ignition, the essential point is the

[9] Garner and Sanders, *Trans. Faraday Soc.*, 1926, **22**, 281.
[10] Finch, *Proc. Roy. Soc.*, 1926, **A111**, 257.
* See also Tizard and Pye[11], p. 1101.
[11] Tizard and Pye, *Phil. Mag.*, 1926, **1** (VII.), 1094.

formation of a centre where the energy of the molecules of high intrinsic energy is not too rapidly disseminated. If conditions are such that diffusion can counteract the establishment of these local centres of ignition, then inflammation does not occur, *particularly* when the thermal coefficient of reaction velocity is not high.

On these views there might well be a difference between "ignition temperatures" found by the adiabatic method and those found by the concentric jet method, even if it were possible to eliminate all the mixing, catalytic and other difficulties involved in it. It is still less to be expected that "igniting temperatures" should correspond to "ignition points."

"Igniting temperatures" are not only dependent on the average temperature of the homogeneous combustible gas mixture and the rate of reaction at that temperature, but on the nature and extent of the reactions at the surfaces.

The values obtained by Dixon and Coward [3] were very little different in oxygen or in air: whereas igniting temperatures as determined in the pot are very considerably lower in oxygen than in air. Rate of loss of heat to the walls is the main factor determining whether reaction rate can rise sufficiently rapidly to autoaccelerate. In the concentric jet apparatus, the loss is not much changed whether the surrounding atmosphere is oxygen or air. With the pot apparatus, however, the walls influence combustion to a far greater extent and the rate is dependent on the concentration of oxygen. Combustion at the walls may be quite considerable (e.g., acetone, p. 261) and yet ignition may not occur. The walls control the rate and at the same time dissipate the heat and average the temperature.

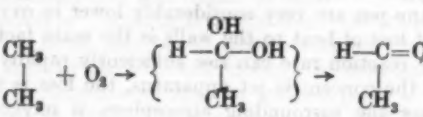
Surface reaction is predominant at the lower temperatures. Ignition is probably set up in a region of high energy in the body of the gas, and any circumstances tending to dissipate heat from such regions raises igniting temperature. If the surface reactions are promoted by increasing the surface (e.g. by addition of glass wool or insertion of plates within the pot), the oxygen concentration is diminished, the reaction products are augmented and the reactions taking place in the body of the gas are hindered (see Part IV, p. 284). Catalysis favours one specific reaction. The surfaces promote reactions which do not proceed so rapidly in the body of the gas. We shall return to this point.

The presence of a thick film of oxide on the surface of the pot which is produced under certain circumstances decreases the amount of surface catalysis and diminishes the dissemination of heat, so that ignition occurs at lower temperatures. The experiment described on pp. 260–1, where the film of oxide is scraped off though left in the pot, supports this view. Since the surface areas do not

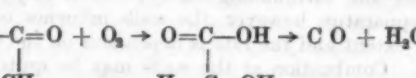
vary greatly for the different types of apparatus that have been in use, the results of determinations of igniting temperature are not very wide apart; for a particular type of apparatus and standard conditions results can be closely repeated. Provided the air supply is sufficient, it is clear from what has been stated as to the mode of combustion that the igniting temperature ought not to be sensitive to change in size of drop or volume of air.

(*b*) *Igniting Temperature and Processes of Combustion.*

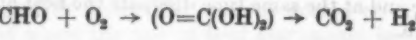
As a combustible mixture is heated in a vessel, reaction becomes appreciable at a temperature which depends on the nature of the surface and the time of contact with the surface. Bone and Stockings [12] showed that Ethane (2 vols ethane and 1 vols oxygen) was burnt in four days in presence of borosilicate glass at 225°, whereas methane did not commence to burn till 300°. It was shown that ethane gave rise to aldehydes, the general scheme of oxidation being given as follows :—



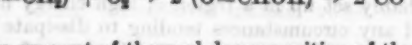
(*a*) $\mathrm{CH_3 \cdot CH_3} + \mathrm{O_2} \rightarrow \{\mathrm{H{-}C(OH){-}CH_3}\} \rightarrow \mathrm{H{-}C{=}O \cdot CH_3} + \mathrm{H_2O}.$



(*b*) $\mathrm{H{-}C{=}O \cdot CH_3} + \mathrm{O_2} \rightarrow \mathrm{O{=}C(OH){-}CH_3} \rightarrow \mathrm{CO} + \mathrm{H_2O} + \mathrm{HCHO}.$



(*c*) $\mathrm{HCHO} + \mathrm{O_2} \rightarrow (\mathrm{O{=}C(OH)_2}) \rightarrow \mathrm{CO_2} + \mathrm{H_2O}$



or $2(\mathrm{O{=}CH_2}) + \mathrm{O_2} \rightarrow 2\ (\mathrm{O{=}CHOH}) \rightarrow 2\ \mathrm{CO} + 2\mathrm{H_2O}.$

A certain amount of thermal decomposition of the ethane, acetaldehyde and formaldehyde is also shown to occur at the same time. It was pointed out that the hydroxylated intermediate products were not detected; for instance, no ethyl alcohol could be found. Experiments indicated that the oxidation of ethyl alcohol was more rapid than that of the ethane, and it was supposed that this stage of the oxidation was passed through so rapidly that very little of such alcohols could be found in the products isolated. Although progressive hydroxylation provides a reasonable view of the process of combustion, more detailed knowledge of the various steps is required. In the body of the gas, the first stage of combustion must be the encounter of a fuel molecule with a specially

[12] Bone and Stockings, *J. Chem. Soc.*, 1904, **85**, 693.

active "oxygen." The consequence could be the formation, though perhaps only momentarily, of a peroxide, which subsequently rearrange or react with other fuel molecules and give rise to aldehydes. It is significant that Bone and Stockings found that the mixture with excess of fuel burnt quicker at lower temperatures than those with excess oxygen. This autocatalysis in the body of the gas and the catalysis at the surface due to adsorbed oxygen give rise to aldehydes which in turn probably form peroxides and are autocatalysed in much the same way, and under certain circumstances may also assist the primary stages of the combustion of the hydrocarbon. The exact nature of these processes has yet to be worked out, but there is considerable evidence that the combustion of both hydrocarbons and aldehydes are autocatalysed through the formation of peroxides. The oxidation of alcohols is not attended by peroxide formation. It is noteworthy that the igniting temperatures of alcohols are slightly higher than those of the corresponding hydrocarbons. Those of the aldehydes are lower. Peroxides are more readily formed in the case of aldehydes and combustion is favoured. The relative igniting temperatures give some information as to the nature of the combustion processes.

Further discussion of these points will be found in Part IV.

(c) *Effect of Pressure.*—In the early stages of combustion, diffusion and other causes can very easily prevent rapid acceleration of the reaction. In adiabatic compression, on the other hand, the effect of diffusion is practically eliminated, the early stages of combustion are passed through quicker, and ignition occurs as soon as the average gain of heat counterbalances the loss. A diffuse area of luminosity signifying the start of ignition is shown in Dixon's photographs[1]; ignition starts in a number of centres nearly simultaneously.

Nothing has yet been mentioned as to the effect of pressure on the temperature of ignition. Thermal conductivity changes little with density, and the ratio of mass of gas undergoing reaction to mass to be heated remains nearly constant, so that increase of total intial pressure should have little influence on ignition temperature. On the other hand, Dixon[8] finds a very considerable influence of pressure on ignition, such that extrapolating the results for methane at various pressures in the concentric jet apparatus to the pressure for adiabatic ignition, the ignition points appear to agree. There is also the experimental evidence of the effect of pressure on the propagation of combustion (Egerton and Gates)[13] which bears on this point. It is certainly suggestive that there should be a

[13] Egerton and Gates, *Proc. Roy. Soc.*, 1927, **114**, 137.

factor influencing ignition which depends on density. It may be an effect due to inequality of mixture, the diffusion coefficient being decreased by increase of pressure, or to greater absorption of radiated energy as the density increases, but still more likely to an increased production of autocatalysts.

5. Igniting Temperatures and Behaviour of Various Fuels in Engines.

This tentative discussion of the subject of ignition indicates that the processes measured by determination of igniting temperatures are similar to those measured by determination of ignition points, but the differences in behaviour between substances *particularly in the initial stages of combustion* are likely to be enhanced.*

The test should be employed for purposes of *comparison* of behaviour of substances, so that any changes occasioned by experimental conditions may be largely eliminated. The usefulness of the method is largely due to the fact that conditions under which vapours are usually ignited are such that contact with surfaces cannot be avoided. In engines combustion is no doubt influenced by preliminary exposure of the gases during compression to the hot surfaces of valves, etc. That there is a close parallel between igniting temperatures and highest compression ratio before detonation sets in can be seen from Table VI. Tendency to detonate is due to much the same influences as tendency to ignite in the pot,

Table VI.

Fuel.	I.T.	H.U.C.R.
Petrol	(460) ..	5·1—5·5
Pentane	515 ..	5·7
Hexane	470 ..	4·8—5·1
Heptane	430 ..	3·7—4·7
Cyclohexane	535 ..	6·0
Benzene	675—710 ..	6·9
Toluene	above 700 ..	>7·0
Xylene	„ „ ..	>7·0
Ether	440 ..	3·5—4·0
Alcohol	515 ..	7·0

viz. the establishment of ignition centres and the effect of diffusion, of catalysts, etc., on these local centres of ignition or propagation. That the mixtures are comparatively slow burning mixtures and particularly *sensitive* to changes of this sort which affect reaction rate have been pointed out by Egerton and Gates.[13]

* Sometimes (*e.g.*, acetone) to too great an extent owing to the predominant surface reactions. The results may indeed then be illusive.

Tizard and Pye[2] have demonstrated that the temperature co-efficient of reaction rate determines delay on ignition and also the tendency of a fuel to detonate. Thus carbon bisulphide does not detonate easily though it has a low ignition temperature, while hydrogen with a high ignition temperature detonates easily. In the first case the temperature co-efficient is small and in the second considerably greater. The effect on igniting temperatures of addition of ether to petrol and that of carbon bisulphide is similar to their effect on the detonation behaviour of petrol in an engine: see Table VII. The behaviour of carbon tetrachloride is also interesting.

TABLE VII.

Igniting temperatures of mixed liquids.

	°C.		°C.		°C.
Petrol	394	.. .. ..	409	.. ..	402
Petrol + 20% CS_2	445	Petrol + 2% CH_3CHO	398	Petrol + 5% ether	409
Petrol + 50% CS_2	494	Petrol + 5% „	398	Petrol + 10% „	409
		Petrol + 10% „	379	Petrol + 20% „	417
		Petrol + 25% „	333	Petrol + 40% „	426
Petrol	437	.. .. ..	445		
Petrol + 0·5% alcohol	437	Petrol + 1% CCl_4 ..	400		
Petrol + 1% „	437	Petrol + 5% CCl_4 ..	335		
Petrol + 2% „	435				

The behaviour of aldehyde and alcohol when added to petrol is also shown. Alcohol detonates less readily than the igniting temperature would indicate. Water vapour raises the igniting temperature of alcohol considerably.*

Though different engines behave differently with the same fuel, in all the experiments with simple, mixed or "doped" fuels there may be said to be general qualitative agreement between the igniting temperatures and the tendency of a fuel to detonate. The main point seems to be that the tendency to detonate is particularly sensitive to influences which change the reaction rate, and that igniting temperatures are also fairly sensitive to such changes brought about by diffusion and by conduction of heat by surfaces or by catalysis. The time factor is of course more important in the case of the engines. The temperature of adiabatic ignition (see Table I) depends primarily on reaction rate, but as explained both the "pot" and the engine enhance the effect of differences of reaction velocity.

* Tanaka and Nagai [14]. We find ordinary undried absolute alcohol ignited at 480°, and specially dry alcohol at 472°.

[14] Tanaka and Nagai, *Proc. Imp. Acad. Tokio*, 1926, **2**, 221.

6. Summary.

1. The ignition point of a substance is defined and its relation to "igniting temperature" discussed.

2. The conditions affecting "igniting temperature" are investigated.

3. Distinction is drawn between the surface reactions and the reactions in the body of the gas. The latter may lead to the establishment of ignition centres, unless dispersed by diffusive influences.

4. The igniting temperatures of various substances are determined, aldehydes are found to ignite at lower temperatures than the corresponding alcohols and hydrocarbons. The effect of mixtures of certain combustible liquids is investigated.

5. The igniting temperature of liquid drops is as a rule lower than that of the corresponding vapour.

6. "Igniting temperatures" are shown to enhance differences in the ignition characteristics of combustible substances and to be related to their knocking characteristics in engines.

III. Note on the Effect of Certain Organic Compounds on the Igniting and "Knocking" Characteristics of Petrol.

By A. Egerton, F.R.S., and S. F. Gates, B.Sc., M.A.*

Much work has been done on the effect of various *organic* compounds on the "knocking" characteristics of petrol (refs. [1] and [2]). The present note provides a brief summary of some of the results of such work, together with further observations which have been made in the course of this investigation.

It is only intended here to set out those facts which any satisfactory theory of anti-knock action must be capable of explaining. The igniting temperature afforded a means of rapidly testing the effect of a large number of different substances. Some of the substances tested are listed at the end of this paper.

Summary of Results.

1. Apart from aryl amines and certain other nitrogenous derivatives (such as diphenylurea) no other substances have been found similarly effective in preventing "knock" except ethyl iodide, quinone, cresol, phenol and diphenyloxide, but none of these are as effective as aniline.

2. Aldehydes, acids, nitrocompounds, nitrates, nitrites, etc., appear to promote "knocking." Most compounds containing halogen promote "knocking" to some extent, but certain compounds—ethylene, dibromide and particularly ethyl iodide—have a slight opposite effect.

3. m-Xylidine is about the most effective of the aryl amines, but about thirty times less effective than an equal volume of lead tetraethyl.

4. Meta compounds are usually slightly more effective than ortho and para compounds.

5. *Diethylamine* is much less effective than *diphenylamine*, monomethylaniline is more, but dimethylaniline less effective than aniline.

6. Quinoline, pyridine and carbylamine are ineffective in comparison with aniline.

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* Paper received April 11th, 1927.

[1] Midgley (and co-workers), *J. Soc. Aut. Eng.*, 1922, **10**, 7, 218, 374, 451 *et seq.* *Ind. Eng. Chem.*, 1922, **14**, 589, 849, 894, *et seq.*

[2] Ricardo, *J. Soc. Aut. Eng.*, 1922, **10**, 305. *Autom. Engineering*, 1921, **11**, various pages.

7. The following figures give a rough measure of the relative effect on "knocking" of iron carbonyl, lead ethyl, nickel carbonyl, aniline, m-xylidine and toluene:—

600, 400, 160, 11, 12, 1.

8. Alcohol, toluene and benzene in mixture with petrol appear to act mainly as diluents raising the H.U.C. according to the quantity added.

9. Ricardo found 50 per cent. carbon bisulphide, in spite of its low ignition temperature, raised the H.U.C. of petrol 6 per cent. This agrees with the effect of such mixtures in the igniting pot.

10. He also discovered the curious fact that ether could destroy the efficacy of the addition of lead ethyl to petrol. If 40 per cent. by volume of ether is added to petrol containing 0·1 per cent. lead ethyl, the H.U.C. of the petrol and lead ethyl mixture is lowered 40 per cent., while the same amount added to petrol alone would only lower the H.U.C. of the petrol 23 per cent. For a 50 per cent. mixture of ether and petrol the effect of the lead ethyl in raising the H.U.C. of the lead ethyl petrol mixture vanishes. However, for larger percentages of lead ethyl, Callendar (3) found that its effect in such mixtures persists. The effect of ether on the *igniting temperature* of petrol shows much the same behaviour (see Table I.):—

TABLE I.

$PbEt_4$.	Petrol.	+2% CH_3CHO.	+5% CH_3CHO.	+10% CH_3CHO.	+25% CH_3CHO.
	409°	398°	396°	379°	333°
+0·1% $PbEt_4$	490	490	490	471	485
Diff. ..	81	92	94	92	152°
		+5% Ether.	+10% Ether.	+20% Ether.	+40% Ether.
	402	409	409	417	426
+0·1% $PbEt_4$	494	494	486	479	471
Diff. ..	92	85	77	62	45°

The effects of additions of acetaldehyde are particularly interesting, exhibiting a contrary behaviour; although acetaldehyde decreases the igniting temperature of petrol, it does not do so to any appreciable extent if lead ethyl is present.

If it were not for other facts, it might have been concluded from this experiment that the effect of the lead ethyl was only to promote surface action, lead ethyl being known to raise the igniting temperature of acetaldehyde alone, and increase in surface action having the same effect. Notwithstanding the other facts (the known decrease in rate of oxidation, etc.), a direct experiment on the point was made in the silica pot. The rise in igniting temperature

on addition of 0·1 per cent. lead ethyl was found to be much the same whether glass wool was in the pot or not, although the presence of the glass wool raised the igniting temperature as much as 170°:—

	I.T.	Difference.
Petrol in empty pot	400°	> 170°
„ in pot+glass wool	570°	> 60°
„ +0·1% $PbEt_4$+glass wool	630°	60°
„ + 5% aniline+ „	630°	

The effect of the anti-knocks on igniting temperature appears, then, not to depend to any great extent on surface, for if their effect were to increase surface action, then they should raise igniting temperature the more, the greater the extent of surface; if, on the other hand, it were to decrease surface action, then they should decrease igniting temperature. Surface oxidation is no doubt decreased to some extent in the presence of metallic anti-knocks, but the main effect appears to be throughout the gas mixture.

TABLE IIb.

Rise in Igniting Temperature of Acetaldehyde (I.T. 225°).

Substance.	Per cent. by vol.	Rise.
Aniline	5 ..	110°
Quinone	5 ..	15°
Diphenylurea	0·5 ..	15°
Hydroquinone	5 ..	75°
Phenol	5 ..	45°

TABLE IIc.

Rise in Igniting Temperature of Valeric Aldehyde (I.T. 320°).

	Per cent.	
Quinone	5 ..	35°

The effect of some organic anti-knocks on acetaldehyde appears to be similar to that which they exert on petrol, except for quinone, but in this case rise in temperature (see Table IIc.) seems to favour its operation (see also p. 276).

11. It is well known that the greater the molecular weight of the normal paraffins the lower is their H.U.C. (and the igniting temperature) and the greater the effect on the H.U.C. of petrol on mixture therewith. Callendar, King and Sims[3] have shown that the lowering produced by such addition is slightly greater than would be expected from the quantity of the paraffin added, the H.U.C. of the pure hydrocarbons being known. Somewhat similarly it has been found that the effect of anti-knocks on the

[3] Callendar, King and Sims, *Engineering*, April 9th, 1926 *et seq.*

H.U.C. of mixtures of petrols and pure hydrocarbons is greater than might be expected from the effects on these constituents alone.

12. Different engines* give different results with different "dopes." Two engines which gave consistent results for aniline and diphenylamine as dopes, showed divergence in behaviour with acetone and with quinone, and also with some of the metallic anti-knocks (*e.g.*, bismuth triphenyl). This was particularly the case on comparing results given by a sleeve valve engine and a tappet valve engine. The inference is that the temperatures within the cylinder control to a large extent the behaviour of the "anti-knocks" (see Table III.).

13. Figures for the effect of a few organic anti-knocks on the "*igniting temperature*" of petrol will be found in Table II*a*. One molecule of lead ethyl is as effective in raising the igniting temperature as about 70 of aniline. Amongst organic substances the only substances found effective at a volume concentration of 1 per cent.

TABLE IIa.

Rise in Igniting Temperature of Petrol.

Substance.	1%.	2%.	5%.	10%.
Aniline	30°	60°	100°	110°
Toluidine	35			
Xylidine	40	65	100	110
α-Naphthylamine	20			
Dimethylaniline	10	20		
Diphenylamine	50	90		
Quinone	30	35		
Acetone	5	10	40	60
Benzene			30	20

were amines, amides and imides, phenol and quinone. Aldehydes as a rule slightly lowered the igniting temperature and most halogen compounds lowered the igniting temperature considerably. Nitrates, nitrites and acidic substances acted in like manner. Diphenylhydrazine was effective but phenylhydrazine ineffective; Dr. Weerman found diphenylamine effective but acetyldiphenylamine ineffective.

No substance found effective in the engine is not effective in the "igniting pot"; the reverse does not always hold, no doubt owing to the different temperature conditions and reaction time available in an engine; for instance, quinone and diphenylamine are both less effective in an engine than indicated by the rise in igniting temperature (see Table III.). The effect of selenium

* With the variable compression engines at Messrs. Ricardo & Co.'s works, Shoreham.

TABLE III.

Engine Behaviour and Effect on Igniting Temperature Compared.

Antiknocks.	Concentration. Per cent. vol.	Rise in I.T.	Rise observed below I.T.	Per cent. rise in H.U.C. Engine A.	Per cent. rise in H.U.C. Engine B. (Sleeve valve).
Benzene	5	30°	30°		0·5
Xylidene	5	100	45		11·1
Acetone	2	10	70	—1·7	
,, ...	5	40	80	—2·7	
,, ...	10	60	80		0·72
,, ...	20	90	(60)	—1·7	
Diphenylamine	1	40	40		
	0·83				5·15
	1·65			7·3	5·15
Aniline	5	100			10·8
	1·76			9·4	
	1·4			7·3	9·5
Quinone	2·0	55	30	Nil.	5·1
	0·75				

diethyl on the igniting temperature of petrol is also considerably greater than engine results would indicate.

14. It is noteworthy that the rise in temperature due to flameless combustion of a mixture of petrol and an organic anti-knock below the igniting temperature is of the same order as that for the organic substance alone (see Part II., p. 262), indicating that the substances tend to promote surface combustion and probably themselves are undergoing rapid oxidation. The effect of the nitrogen anti-knocks is very different in this respect from that of the metallic anti-knocks; the latter decrease the rise in temperature below the igniting temperature, the former tend to increase it. However, the general behaviour of organic anti-knocks on hydrocarbons, aldehydes, etc., seems to be similar to that of the metallic anti-knocks (see experiments on effect of surface and Table II*b*.).

As mentioned in Part I., p. 254, metallic anti-knocks decrease oxidation as shown by analyses of the oxygen and CO_2 content of the air used and of the products formed. It has also been shown* by withdrawing a portion of the charges at the end of the compression stroke through a valve which is momentarily opened, and also by collecting alternate charges instead of firing them that the "doped" spirit is much less oxidised than the ordinary spirit, the proportion of alcohols and aliphatic aldehydes being considerably greater in the condensed liquid in the latter case. (See Summary of Experiments, Table IV.)

* With the variable compression engines at Messrs. Ricardo & Co.'s works, Shoreham.

TABLE IV.

	Time of run. Hrs.	Volume of condensate. c.c.	
Aromatic free spirit ..	1¼ ..	5 ..	Aliphatic aldehydes
+0·13% $PbEt_4$	1 ..	3 ..	No aldehydes
Light Burmah	— ..	7 ..	4·3% alcohols, and aldehydes
*0·11% $PbEt_4$	— ..	7 ..	1·4% alcohols, very little aldehyde

The main result of these investigations is that some organic substances appear to act like metallic anti-knocks, but owing to their own decomposition and combustion their effect is necessarily very much less and determined to a great extent by the temperature.

SUMMARY.

The paper contains a summary of results of experiments on the effect of various organic substances on igniting temperatures and on the knocking characteristics of fuel.

TABLE V.

S=soluble; s.s.=slightly soluble; p.s.=partially soluble; i=insoluble. Organic bodies tested as dopes at a concentration of 1% except where stated.

Substance.	Concentration or sol.	Effect.
Hydrocarbon—		
Benzene	25% ..	40° C.
Toluene	25% ..	50° C.
Xylene	25% ..	50° C.
Tetrahydrobenzene	s. ..	Nil.
Diphenylmethane	s. ..	,,
Triphenyl methane	s. ..	,,
Mesitylene	s. ..	,,
Fluorene	s. ..	—10
Tetrahydronaphthalene	s. ..	Nil.
Naphthalene	p.s. ..	,,
Acenaphthene	s. ..	,,
Chrysene	s.s. ..	,,
Diphenyl	s. ..	—
Anthracene	p.s. ..	—
Phenanthrene	s. ..	—
Paraffin	5% ..	—
Turpentine	.. ..	—
Dipentene	.. ..	—
Diethyl malonate	s. ..	—
Glycocoll	i. ..	—

Substance.	Concentration or sol^{y}.	Effect.
Phenols, etc.—		
Phenol	s.	+20°
Resorcinol	s.s.	Nil.
Pyrocatechol	s.s.	„
Hydroquinone	s.s.	„
α-Naphthol	s.s.	„
Thymol	s.	„
Metol	s.s.	„
Eugenol	s.	„
Ketones, Quinone, etc.—		
Acetophenone	s.	—
Benzil	s.	—
Dimethyl-pyrone	p.s.	—
Benzophenone	s.	—
Acetone	5%	—
Aldehydes—		
Valeric Aldehyde	s.	−20°
Piperonal	p.s.	Nil.
Acetaldehyde	s.	„
Paraldehyde	s.	−10°
Benzaldehyde	s.	−10°
Amylalcohol	s.	—
Anisole	s.	—
Ethers, etc.—		
Diphenylether	s.	−15°
Sulphanilic acid	i.	—
Valeric acid	s.	−20°
Benzoyl peroxide	s.s.	—
Mesityl oxide	s.	—
Acetic anhydide	s.	—
Camphor	s.s.	—
Coumarin	p.s.	—
Aesculin	s.s.	—
Rhodamine	p.s.	—
Iodoform	10	−50°
Carbon tetrachloride	10%	−100°
Acetylene tetrabromide	—	−140°
Triphenyl methyl bromide	—	Negative
Carbon bisulphide	50%	+ 40°
Nitrogen Compounds—		
Pyridine	s.	—
Quinoline	s.	—
Acridine	s.s.	10°
Carbazole	i.	—
Diphenyl carbazide	i.	—
Piperidine	—	10°
Di-phenylurea	s.s.	20°
Aniline	5%	90°
	1%	30°
Toluidine	s.	30°

Substance.	Concentration or solv.	Effect.
Xylidine	s.	40°
Orthobromaniline	—	Negative
Benzal aniline	s.	—
Dimethylaniline	5%	30°
Diethylamine	s.	—
Diphenylamine	—	ca 40°
Triphenyl methylamine	—	—
Acetyl diphenylamine	—	—
Phenyl hydrazine	s.	−10°
Diphenyl hydrazine	p.s.	−25°
α-Naphthalamine	s.	20°
β-Naphthylamine	s.	Positive
Metaphenylene-diamine	i.	—
Toluylene diamine	i.	—
Dimethylglyoxime	s.s.	—
Formamide	i.	—
Aldehyde ammonia	i.	—
Isopropyl nitrate	—	−20
Phenyl hydroxylamine	—	Negative.
Acetanilide	i.	—
Azobenzene	—	—
Azoxybenzene	—	Negative
Benzidine	i.	—
Nitrosobenzol	—	Negative
Phthalimide	s.s.	+10
Nitrophenol	s.	—
Nitroanisol	s.	—
o-Anisidine	—	+
m-Anisidine	—	+
p-Anisidine	?	40°
p-Phenetidine	—	30°
8-Aminoquinoline	—	+
o-Bromaniline	—	−10°
Phenacetine	—	—
Pyramidon	—	—
Dimethyl 3-5 pyrazol	—	—
Diazobenzolimide	—	—
Quinone	s.	+25
Anthraquinone	s.s.	—
Quinhydrone	s.s.	+15
Benzoyl acetone	s.	—
Fluorenone	s.s.	—

Note.—Some of the above substances were tested in the Laboratory de Bataafsche Petroleum Maatschappij in Amsterdam by Dr. Weerman.

IV.—Theories of Antiknock Action.

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In the foregoing Papers information has been collected on the behaviour of various "antiknocks" and their behaviour on various fuels. The facts so gleaned lead to an explanation of the action of "antiknocks" as negative catalysts. Further study and quantitative experiments are needed to develop the ideas which we put forward, but the work which has been described narrows the problem down to a smaller range of more soluble and definite problems. Some of the other theories put forward in explanation of the action of "antiknocks" are here briefly reviewed and criticised.

I.—Summary of Main Facts.

(1) It was very important to establish that rise of igniting temperature due to "antiknocks" and their effect in the engine have the same chemical cause. This seems definitely proved. Physical conditions in the engine (particularly temperature and time) may, however, modify the behaviour of a given antiknock. No antiknock has been found which does not influence the igniting temperature. With the same antiknock, engines may differ somewhat in the compression ratio at which they knock. The effect which the igniting temperature would suggest is not always followed by engine behaviour.

(2) Even when fuel and antiknock are completely in the gaseous state, it is established that metallic antiknocks will suppress detonation and raise igniting temperature.

(3) Rise of igniting temperature produced by organo-metallic antiknocks is attended by reduction in rate of combination of fuel with oxygen. In presence of antiknocks less oxidation occurs during the compression stroke in an engine.

(4) The metal atom of an organo-metallic antiknock is the main active constituent.

(5) Only metals with certain oxidisable properties are effective. Influence of temperature and concentration of oxygen has an important bearing on their behaviour.

* Paper received April 11th, 1927.

(6) Organic amines, quinones, phenols (certain ureas and nitriles) are the main types of organic compounds which have been found effective. All the substances found effective have high boiling points and igniting temperatures. On admixture with petrol an increase in temperature is observed prior to ignition in the pot, contrary to the behaviour of the organo-metallic antiknocks.

(7) The combustion of an aldehyde is greatly affected by antiknocks, but that of an alcohol hardly at all.

(8) Compounds with methyl groups, long chains, etc., have generally lower igniting temperature and are more affected by antiknocks; on the other hand, the reverse seems to be the case for benzene, toluene and xylene.

(9) Detonation experiments[1] show that rate of combustion is unaffected by organo-metallic antiknocks up to initial temperatures of 230° C, and initial pressure of 130 lbs. The conditions different from engine conditions are mixture strength, temperature and turbulence. The composition of the weakest charge that would give detonation at engine pressures in the 150 cms. long tube was for pentane approximately $1\,C_5H_{12} : 8O_2\,15N_2$, which is considerably stronger than an engine mixture. The rate of combustion of the comparatively weak mixtures used in engines may be somewhat diminished by antiknocks, but not to such an extent that the indicator diagram for a given engine with doped fuel exhibits an appreciable difference from that of an undoped, at the same compression ratio below the highest useful compression ratio for the fuel alone.

(10) There are other points, such as the opposite behaviour of rich benzene and rich hexane mixtures on explosion in a bomb at high initial temperatures (Fenning[2]), the effect of addition of ether to doped petrol, the effect of the addition of hexane to certain petrols, and the effect of air-inlet temperature on certain doped fuels, which any suggestion as to the mode of action of antiknocks has to account for.

II.—Conclusions.

Broadly, the following conclusions can be drawn regarding primarily the behaviour of organo-metallic antiknocks:—

(1) From the detonation experiments it is clear that antiknocks do not affect processes of rapid combustion, but only those which are particularly sensitive to change of reaction rate.

(2) From the temperatures at which antiknocks commence to operate in the igniting pot, and from the decomposition experi-

[1] Egerton and Gates, *Proc. Roy. Soc.*, 1927, **114**, 137.
[2] Fenning, Repts. Aer. Aes. Comm., No. 979.

ments (see Part I, p. 254) it is clear that their effect is determined within certain temperature limits, which depend on the nature of the fuel and the antiknock.

(3) In the presence of metallic antiknocks, the rate of oxidation and generation of heat in the processes of slow combustion are less than without the antiknock; the initial processes of combustion *must* therefore be retarded.

(4) Only a very small proportion of antiknock being necessary to retard oxidation, presumably it must be acting as a negative catalyst. Will not the usual explanation of a negative catalyst suffice in this case—namely, the removal of a positive catalyst?

The problem reduces to that of (*a*) finding a process of negative catalysis controlling the preliminary stages of combustion, and (*b*) showing how the process is effective in preventing knocking.

(*a*) *Processes of Negative Catalysis.*—On Bone's[3] hydroxylation theory of combustion a hydrocarbon reacts with oxygen, is hydroxylated to an alcohol, then to an aldehyde, etc. At each stage the substances may also break down and oxidise direct to water and oxides of carbon. A certain amount of thermal decomposition may also occur during the process, giving rise to simpler products, which in turn oxidise in a similar manner. Bone[4] extended his researches on slow combustion to explosive mixtures, and evidence was obtained that even during detonation the oxidation of the molecule went through similar stages only with exceeding rapidity.

Now it is known that in these processes of combustion, hydrogen peroxide[5] and other peroxides[6] may be formed in small quantity. We shall assume that such products autocatalyse both the initial oxidation of the hydrocarbon, and perhaps the aldehyde oxidation. In the absence of such products neither the initial oxidation of the hydrocarbon, nor the decomposition and oxidation of any aldehyde which happened to be formed would be promoted. So that if we assume that the antiknock removed this catalyst as soon as it commenced to form, combustion would be retarded. Thus the outline of the view of negative catalysis we have adopted is that the antiknock removes the product or products of oxidation which would otherwise be able to catalyse the initial stage of the combustion. Combustion will therefore not take place till higher temperatures are reached. This hypothesis, which we shall develop in the following pages, offers explanation of the extraordinary small quantity required to be effective, and the general behaviour of antiknocks with different types of fuel.

[3] Bone and Wheeler, *J.C.S.*, 1902, **81**, 535.
[4] Bone and Drugman, *J.C.S.*, 1906, **89**, 660, 1614.
[5] Traube, *Ber.*, 1882, **15**, 663.
[6] Bach, *Compt. rend.*, 1897, **126**, 951.

Bone's conclusions as to the combustion of ethane were given in Part II., page 268. Attention was drawn to the fact that ethyl alcohol was not isolated. Bone and Stockings stated that the rate of oxidation of ethyl alcohol at the temperatures which were employed was sufficiently great to prevent its appreciable accumulation. On the other hand, it is possible that oxidation may also proceed direct from hydrocarbon to aldehyde.

$$R{\cdot}CH_2 + O_2 \rightarrow R{\cdot}CHO + H_2O.$$

The point we wish to make is that perhaps it is not quite clear what is really the first step in the process of combustion of even so simple a hydrocarbon as ethane.

Combustion becomes appreciable at a certain temperature, which depends for a given mixture on the nature and state of the walls of the vessel. No doubt at first such reaction occurs almost, if not entirely, at the surface. The surface exposes an active layer of oxygen, which presents possibility of combination with a sufficiently active fuel molecule. The oxidation of alcohols to aldehydes occurs readily at the surface of certain catalysts (e.g., silver), but there is for most surface combustion of this sort much decomposition going on at the same time. It is, in fact, difficult to elucidate exactly what reactions are most favoured by the catalyst: whether, for instance, two atoms of oxygen are involved in the direct oxidation of a hydrocarbon to an aldehyde, or whether that is less frequent than stages of hydroxylation by single oxygen atoms. Whatever the precise nature of the surface catalysis, we think that reaction in the body of the gas does not occur till the oxygen is presented to the fuel molecules with which they suffer encounter in something the same active state as they exist on the surface. This is occasioned by formation of oxidation products, such as peroxides, which thus become autocatalysts. When sufficient catalyst is present and diffusive influences are not too prevalent, reaction may become rapid enough to set up centres of ignition in the body of the gas. Surface catalysis avoids the formation of these peroxides, and in fact destroys them; and so conditions that promote surface combustion tend to raise igniting temperature. There is thus an essential difference in surface combustion and combustion in the body of the gas, though really the processes in both cases are catalytically similar.

Further, substances which provide active oxygen, organic nitrocompounds, nitrites, peroxides, etc., tend to lower the igniting temperature. At high wall temperatures reaction may be fast enough and ignition may spread out from the walls (e.g., in the case of methane where ignition seems to proceed quietly and somewhat

indistinctly at a somewhat indefinite temperature, when the walls are fully red hot), but for substances igniting at low temperature ignition often occurs explosively (particularly in oxygen with considerable delay). Under such circumstances it is probable that ignition occurs in the body of the gas from the centres of high concentration of autocatalyst. The fact that a drop ignites at a considerably lower temperature than the corresponding vapour is due probably to the accumulation of oxidation products in the drop, and therefore the ease with which ignition centres can be formed in the immediate neighbourhood of the drop.

If the hydrocarbon by encounter with oxygen molecules of sufficient energy may form peroxides, it would seem that they should be formed still more favourably by aldehydes, and this might be a reason for the ease with which aldehydes can be ignited, and for the great effect of antiknocks upon them as will be considered further on. A difficulty arises here. Firstly, aldehydes are readily formed by the surface reactions, and such products becoming mixed with the rest of the gas should lower the igniting temperature; and, secondly, a small quantity of aldehyde added to a fuel should lower the igniting temperature of the mixture. It is found, however, that considerable quantity has to be added before this occurs. This latter fact, however, supplies a clue to the difficulty. Unless the concentration of the aldehyde is sufficient its presence makes only a slight difference to the amount of peroxide present or to the ease with which an ignition centre is set up, since for the formation of these peroxides it is necessary that the concentration of the substance from which they are formed should be high. Increasing the concentration of the oxygen also favours the production of these peroxides and so lowers igniting temperatures.* It is noteworthy that Bone and Stockings found that surface combustion was very much diminished unless the concentration of the fuel was high. Thus $2C_2H_6+1O_2$ commenced to burn at 225° C., while $C_2H_6+3{\cdot}75O_2$ only burnt very slowly at 300° C. The surface of the vessel determines the combustion in this case, and being already saturated with active oxygen, increase of oxygen concentration does not excite combustion as it would do in the body of the gas by formation of peroxides. It is also significant that increase of surface raises the igniting temperatures of aldehydes markedly: the surface tends to destroy the peroxides.

Our discussion leads us, therefore, to the view that peroxides are formed which autocatalyse the combustion of the fuel, but only

* See p. 291 for further consideration of this point.

the peroxides of the combustible which is at high concentration are formed in sufficient quantity to be effective. Without the small quantity of autocatalyst, oxidation does not get started till much higher temperatures. Temperature alone may then provide sufficient active oxygen to set up ignition. Secondly, in order to establish an ignition centre, dispersal of the active products and of heat must be avoided so that the concentration factor is here again important.

Much remains to be done to establish where the oxygen commences to attack a fuel molecule and what the actual products are that influence the initial stages. For instance, in the case of a higher paraffin, is the centre of the chain attacked more readily than the terminal groups? In the case of benzene is the formation of diphenyl a preliminary to the formation of peroxides, or can phenols and quinones be first formed? Possible transformations are very great in the case of complicated molecules as thermal decomposition can occur at the same time as oxidation, but it is clear from the work of Hinshelwood[7] on the rate of decomposition of aldehydes, acetone, etc., that anyhow for these substances thermal decomposition is a much slower process than that of oxidation at the same temperature.

We will consider now the influence of antiknocks on these processes of combustion in more detail. When a metal vapour such as potassium enters the igniting pot, after comparatively few encounters with oxygen molecules constituting the atmosphere of the pot, combination to KO_2 and thence to K_2O_4 must have occurred. For the reaction $2K_2O_4 \rightleftharpoons 2K_2O_3+O_2$ the dissociation pressure would be certainly less than 150 mms. (the partial pressure of oxygen) at 450° C. (Kraus and Whyte[8] give the figure 0·17 mm. at 300° C.) The peroxide of the metal could therefore be reformed although it might have suffered mutual reduction* with the fuel peroxide. It is thus possible for a small quantity of metal peroxide catalyst to inhibit the formation of those peroxides which tend to start ignition.

In the case of sodium the following oxides are described:—(Na_2O_2, Na_2O_3, Na_2O_4, and Na_2O); the equilibrium $Na_2O_2 \rightleftharpoons Na_2O+\frac{1}{2}O_2$ does not appear to have been investigated, but it is known that the monoxide will give Sodium and Sodium peroxide above 400° C.

The equilibrium for calcium peroxide has been measured by Bergius; at 400° C. the dissociation pressure is 150 mms; therefore, one would expect calcium to have a very feeble effect. On

[7] Hinshelwood, *Proc. Roy. Soc.*, 1926, **111**, 380; **113**, 221.
[8] Kraus and Whyte, *J. Amer. Chem. Soc.*, 1926, **48**, 1781.
* E.g., in the manner $H_2O_2+Ag_2O=2Ag+H_2O+O_2$.

the other hand, lead oxide $Pb_3O_4 \rightleftharpoons 3PbO+\frac{1}{2}O_2$ has a dissociation pressure of only 10 mms. at 400° and 50 mms. at 500° C. One would expect therefore that lead would be particularly effective.

Manganese dioxide $2\ MnO_2 \rightleftharpoons Mn_2O_3+\frac{1}{2}O_2$ has a dissociation pressure of about 20 mms. at 380° C., but at 480° the pressure is 200 mms. It would therefore not be so effective as lead.

Figures are not apparently available for other metals which exhibit antiknocking properties, but the following notes are relevant:—

The reaction $Tl_2O_3 \rightarrow Tl_2O+O_2$ is appreciable at a low red heat and is complete at 800° C.

On burning cadmium metal a small quantity of cadmium peroxide is detectable in the oxide smoke, whereas zinc does not give any peroxide in the same circumstances.

A number of peroxides of bismuth are known.

Antimony pentoxide dissociates into the trioxide and oxygen at 440° C.

Iodine pentoxide decomposes above 300° C.

In practically all other cases the oxides are all too stable (CuO, B_2O_3, ZnO, MgO, Al_2O_3, CeO_2) or too unstable (Ag_2O, HgO) or are not formed at all (Au, Pt).

It is, in fact, just the metals which have peroxides with a stability indicated by the above figures which are effective as antiknocks. This correspondence between the behaviour of the oxides of metals and their character as antiknocks is so close that the assumption as to their mode of action seems justified.

It is essential that the peroxide should be in a molecular condition throughout the body of the gas.* In the case of iron and nickel carbonyls the metal is formed in a very finely divided state, which probably becomes rapidly oxidised. These oxide particles condense oxygen on their surface—practically becoming peroxide—the oxygen being in a state in which it is catalytically active. The catalytic activity of ferric oxide is well known, and it does not seem improbable that the special antiknock effect of these metals produced in this particularly finely divided condition may not be explicable in this manner.

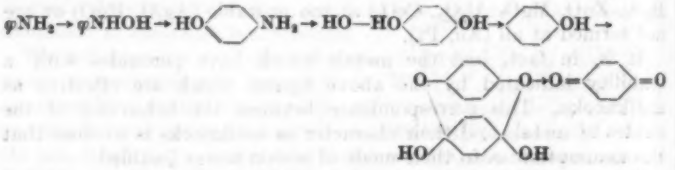
In the case of selenium (and tellurium to a less extent) the effect in the pot is much greater than in the engine. Selenium trioxide is apparently not formed from the dioxide by heating in air, the latter being stable at a red heat; but it is noteworthy that the dioxide is very easily reduced in the presence of carbon compounds,

*It is for this reason that such non-volatile substances as lead oleate are comparatively ineffective, the oxide would be produced in a conglomerate form.

and it is probable in a combustible mixture there is a definite equilibrium between the selenium and its dioxide. In the engine pressure would shift the equilibrium towards the dioxide, reducing the antiknocking effect.*

It should perhaps be mentioned that the stability of the anti-knock compound itself is of importance. If it is not completely broken up at the temperature required then it is not so likely to be so effective; for instance, aryl compounds are less effective than alkyl. The influence of the nature and concentration of the fuel itself would also have a bearing on the extent of the thermal decomposition of the compound. (See p. 292.)

Amongst the organic antiknocks it has been found that amines, nitriles, phenols, quinone and certain iodides are the types of substances which are found effective as antiknocks. Do the same ideas which have been used to explain the behaviour of metallic antiknocks cover the behaviour of these substances? These types of substances can give rise to peroxides (Bach).[9] Aniline may oxidise somewhat as follows:—



Similarly phenols give rise to quinones, which in turn can give rise to temporary higher oxides. A great deal is not known as to the peroxidation of organic substances, but that there are such substances, which may have a certain stability at the temperature 300°C—500° C. required is more than likely.[10] These peroxides could thus act like those of the metals and react with and destroy the peroxides produced by the fuel. Mere reduction is insufficient, the negative catalyst being not then regenerated. These organic antiknocks are very much less effective than the metallic antiknocks, because they themselves suffer breakdown and oxidation to a considerable extent; a larger quantity of negative catalyst is thus required for the same effect as is obtained in the case of a satisfactory metallic antiknock. The pot experi-

* Further investigation is necessary on this point, but the effect of CS_2 in raising H.U.C. and igniting temperature of petrol is in agreement with this suggestion. The effect is naturally much less in the case of sulphur than selenium for the same quantity.

[10] Straudinger, *Ber.*, 1925, **58**, 1075.

ments described in Pt. III, p. 277, where a rise in temperature was obtained in the presence of organic antiknocks, indicate that the negative catalyst itself suffers combustion to a great extent.

Now we derive considerable support for these ideas from the work of Moureu and Dufraisse.[11] In a long series of papers they have described experiments on the inhibition of oxidation of aldehydes, unsaturated hydrocarbons, and other organic substances, by such substances as phenols, amines, quinone, certain sulphur and iodine compounds—in fact, just those types of substances which are effective as antiknocks. The oxidation occurs in the liquid state at normal temperatures. For instance, one molecule of hydroquinone in 40,000 of acrolein arrests the oxidation. The work, which is an extension of that of Engler and Wild[12] utilises a similar explanation of the mode of action of these inhibitors. A being the oxidisable substance, and B a catalyst, Moureu and Dufraisse explain their results as follows :—

$$(1)\ A+O_2 = A[O_2]$$
$$(2)\ A[O_2]+B = A[O]+B[O]$$
$$(3)\ A[O]+B[O]=A+B+O_2.$$

The oxidisable substance forms a peroxide $A[O_2]$ which would ordinarily proceed to give $A[O]\rightarrow AO$ (stable), but in the presence of the catalyst B, which can form a peroxide B[O], A [O]+B[O] mutually destroy each other according to equation (3) above. Thus, if A be an aldehyde and B be a phenol, then :—

aldehyde + O_2 = aldehyde [O_2]
aldehyde[O_2] + phenol = aldehyde[O] + phenol[O]
and aldehyde [O] and phenol [O] = aldehyde and phenol + O_2

so that oxidation of the aldehyde is stopped.

Alternatively, the process may be represented :—

aldehyde + O_2 = aldehyde [O_2]
phenol + O_2 = phenol [O_2]
aldehyde [O_2] + phenol [O_2] = aldehyde + phenol + $2O_2$.

If B [O] tends to react with A rather than with A [O], giving A [O]+B, and A [O] becoming AO (stable), B [O] will then be acting as a positive catalyst instead of a negative catalyst. Whether the peroxide acts as a positive or as a negative catalyst depends on the oxygen pressure and the stability of the peroxide B[O]. The importance of this point has been demonstrated in a particular case by Job[13] and Goard and Rideal[14] in their work on autoxi-

[11] Moureu and Dufraisse, *Compt. rend.*, 1922, **17**, 258 *et seq.*
[12] Engler and Wild, *Ber.*, 1897, **30**, 1669 *et seq.*
[13] Job, *Ann. Chim. Phys.*, 1900, **20**, 205.
[14] Goard and Rideal, *Proc. Roy. Soc.*, 1924, **105**, 135.

dation of solutions of potassium arsenite and of sugars, and the effect of cerium salts thereon. If the oxygen pressures of the compounds involved follow the order :—

A	B	AO·BO	BO_2
acceptor (sugar)	inductor (cerous salt)	equilibrium mixture	peroxide (per.-ceric salt)

then an indefinite amount of sugar can be oxidised by the aid of the cerium catalyst, for the peroxide will be reduced by the sugar to the cerous state if plenty of the former is present. The cerous salt peroxidises again and so on. If, on the other hand, the order is :—

B	A	AO·BO	BO_2
inductor (cerous salt)	acceptor (potassium arsenite)	equilibrium mixture	peroxide (per.-ceric salt)

then the per-ceric salt is reduced by the potassium arsenite to the intermediate ceric oxide BO until the pressure is reduced to the value at which AO and BO can exist together, and as the arsenite cannot reduce the oxide BO to B, BO_2 cannot be reformed and the reaction will stop.

We have quoted the above as an example of the importance of oxygen pressure on the course of the catalysis. In our case the inductor is the autoxidant formed from the fuel itself :—

A	+ B[O_2]	⟶ A[O] + B[O]
hydrocarbon (acceptor).	Fuel peroxide.	

B here may be the radicle A, so that 2[AO] would result. (Baeyer and Villiger[15] proved the production of benzoyl hydrogen peroxide in the oxidation of benzaldehyde.)

If B, fuel	A', anti-knock	A'[O], anti-knock peroxide	B[O], oxidised fuel	B[O_2] is the order fuel peroxide

of oxygen pressure of the compounds taking part, then B(O_2) is destroyed by the antiknock and cannot be reformed, so that the catalyst is removed. If, however, the external oxygen pressure is increased, the antiknock peroxide and oxidised fuel equilibrium is disturbed, and the substance B[O_2] can be reformed : the combustion of the hydrocarbon being promoted.

[15] Baeyer and Villiger, *Ber.*, 1900, **33**, 838, 1569.

Although this point has not been quantitatively investigated, it is clear that some mechanism of this sort holds sway, for antiknocks such as lead ethyl have no effect on the igniting temperatures of hydrocarbon fuels, or of aldehydes, in an atmosphere of oxygen. It is interesting to note, however, that whereas they have very little effect on alcohols in air, they have an appreciable effect in raising their igniting temperatures in oxygen, as the following figures indicate. (See also Tanaka and Nagai.[16])

Substance.	Air.*	Air in presence of 0·1% $PbEt_4$	O_2	O_2 in presence of 0·1% $PbEt_4$
Petrol	550° C.	575° C.	320° C.	320° C.
Acet-aldehyde ..	470	630	175	175
Alcohol	485	490	415	430

We have already pointed out that the concentration of the fuel is also important; the peroxide is not formed to a sufficient extent to be effective if the fuel is diluted. For instance, the oxidation of alcohols is not appreciably catalysed by the aldehydes produced, the admixture of a fuel of low-igniting temperature has little effect on that of a higher one unless a large proportion is present. The point is also exemplified by the difference of igniting temperatures of drops and vapour. It is interesting to note that in a series of derivatives of the same hydrocarbon radicle, the effect of an antiknock is greater on that derivative which possesses the lower igniting temperature, so that the resulting igniting temperatures tend to approximate, the inference being that production by and the concentration of autoxidants is greater in the lower igniting derivatives. This is also true of the members of a homologous series, the lower members igniting at a higher temperature than the higher members.

These views also suggest that the several oxidation products of combustible substances may mutually counteract: a combustible may not only produce a peroxide inducing combustion, but also an anti-oxidant counteracting the effect of the peroxide. Thus the effect of benzoyl peroxides formed in the combustion of benzene —through di-phenyl and its subsequent oxidation perhaps—may be counteracted by quinones, etc., also formed during oxidation. Such a view might explain the higher igniting temperatures obtained for toluene and xylene, as well as the effects mentioned on p. 282, where benzene-air mixtures heated to 2–300° C. were found to detonate less readily than those at normal temperature.

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[16] Tanaka and Nagai, *Proc. Imp. Acad. Tokio*, 1926, **2**, 221.

* These figures are high, owing to the small size of the pot used for these particular experiments.

It must be pointed out that the experiments of Moureu and Dufraisse were made in the liquid state at normal temperatures. Oxidation did not occur in the vapour above the liquid, otherwise oxygen would have continued to be absorbed even when an inhibitor was added to the aldehyde undergoing oxidation. Here, again, it is a question of concentration of acceptor. We consider similar reactions can occur in the vapour but at higher temperatures. The oxidation of benzaldehyde in the liquid state has also been studied by Reiff,[17] the view being adopted that the reaction is purely a surface one depending on the rate of diffusion of oxygen to the active wall surface, and that the activity of the walls is affected by the presence of inhibitors. We have already pointed out, in discussing surface combustion, that the walls may behave in a similar manner to autoxidants, so that such a conclusion does not invalidate the general scheme of catalysis devised primarily by Engler and Wild and adopted by Moureu and Dufraisse. Further, the evidence is strong that at higher temperatures in a droplet where the only surface is between liquid and air, the effects of induced and inhibited oxidation can be observed. Since autoxidation in the vapour at normal temperatures is not apparent in the vapour, it is not surprising that it is greater in the liquid than in the vapour at higher temperatures; hence the lower-igniting temperature of the droplets than the vapour.

Moureu and Dufraisse found among nitrogen compounds that secondary amines such as monomethylaniline were more effective as inhibitors than primary (e.g., aniline) or tertiary (e.g., dimethylaniline), that pyridine and quinoline were ineffective, that *p*-acetophenetidine was ineffective though phenetidine was effective. These and other points are in precise correspondence with the behaviour of such substances as antiknocks, and it is quite clear that the phenomena are closely related.

Ether gives rise readily to ether peroxide $CH_3—CH(—O—C_2H_5)—O—O—H$ (Clover[18]): in spite of this, as ether is added to petrol the igniting temperature slightly rises, the addition of antiknock neutralising this effect. These and other peculiarities of mixed combustibles can be explained in terms of the views put forward.

The above is a general discussion of the problem of antiknocks; but much, of course, remains to be done in testing quantitatively the explanation suggested and in extending the field of investiga-

[17] Reiff, *J. Amer. Chem. Soc.*, 1926, **46**, 2893.
[18] Clover, *J. Amer. Chem. Soc.*, 1922, **44**, 1107.

tion, particularly in connection with the control of the oxidation of organic substances.

(*b*) *Prevention of "Knocking."*—It remains now to show how this process of negative catalysis can bring about the reduction of the tendency of a given fuel to "knock" in an engine.

For the occurrence of ignition the importance of the establishment of ignition centres and the ease with which they may be dispersed has already been discussed. The removal by antiknock of the autoxidant in the initial stages of combustion in the manner described in the preceding paragraphs is sufficient to explain the resulting rise of the igniting temperatures.

In an engine cylinder the turbulent charge suffers a certain amount of combustion during compression prior to ignition, and there is time to form those catalysts which favour combustion. The compression time is of the order of 1-100th sec., and the temperature at the end of the compression stroke is of the order of 450° C. In front of the combustion zone also reactions take place in the unburnt gas prior to ignition which involve autoxidation in a similar manner. The more active oxygen available the quicker the reaction rate will increase. It has to rise very rapidly for detonation to occur.* The same processes that delay the setting up of ignition in the pot delay the setting-up of detonation in an engine. The composition of the mixture in an engine is near a "limiting detonation" mixture. "Limiting detonation" mixtures are those whose reaction velocity are only just great enough during the time of passage of a detonation wave to provide the reaction heat to maintain it. A very small change in composition of the mixture—or state of reactivity of the mixture—will modify very greatly the tendency to detonate. Wendlandt[19] has shown for hydrogen-air and carbon monoxide-air mixtures that the velocities of propagation of combustion in the limiting mixtures are very sensitive to change of composition. Whether or not true detonation does occur in an engine charge has not yet been finally settled. Our experiments (1) showed that mixtures as dilute as those used in engines cannot be detonated in a narrow steel tube 150 cms. long by 1·5 cms. diameter even at 9 atmos. pressure or even at 230° C. They also indicated that the setting up of a true detonation

* In discussing with Mr. H. T. Tizard, F.R.S., our experiments[1] which indicate that detonation starts in a region of high pressure slightly in front of the combustion zone, he suggested that a short delay before inflammation might be occurring just as in adiabatic ignition, and that, unless the delay were shorter than the time taken for the combustion zone to travel to the point of autoignition, no detonation would be observed. This view of the setting up of a detonation wave has much to commend it.

[19] Wendlandt, *Z. physical Chem.*, 1924, **110**, 637; 1925, **116**, 227.

is more violent than an engine cylinder could long stand. Conditions in an engine, however, may be such that local detonation—without transmission of a detonation wave—might occur in a portion of the charge. We may mention here that our more recent experiments indicate that although auto-ignition well ahead of the combustion front did not occur in the long narrow tube even at the highest pressure, yet there is evidence of it in a short, fat bomb 20×12 cms. using acetylene mixtures giving a knocking sound on explosion. This difference is explained by the great heat loss which would occur in the long tube compared with the short fat bomb, which would disfavour auto-ignition in the former. The resulting photographs of explosions in the short bomb show a check in the progress of the flame, followed by enhanced combustion. Whether knocking be "auto-ignition" or "local detonation," both would be greatly affected by any change in the rate of the initial stages of the reaction, and would therefore be influenced by antiknocks.

When once rapid combustion is established there is plenty of heat available for the ignition of the next layer of gas, and as antiknocks influence mainly the slow initial processes of combustion, their effect is not apparent under such conditions. But it might be expected that some effect would be observed on the rate of propagation of slow combustion. We have recently established that lead ethyl will slow down the velocity of the flame in weak pentane-air mixtures. It must be emphasised, however, that it is the effect of antiknocks on the tendency to ignite that is the important point in the suppression of knocking.

The presence of hot surfaces, the rate of loss of heat, the extent of preliminary combustion and the time available for it, all have a bearing on the tendency to "knock" in different engines, but there is no need for further discussion of these points in this Paper. The maximum flame temperature and the state of the charge as modified by the various preliminary reactions determine the "knocking" characteristics of the fuel for a given engine.

3.—Other Theories of Antiknock Action.

The following pages briefly discuss certain other theories of antiknock action which have been put forward:—

(1) *Nuclear Drop Theory.*—Callendar[30] * put forward the suggestion that the presence of nuclear drops in the charge facilitate

[30] Callendar, King and Sims, *Engineering*, April 9th, 1926 *et seq.*

* Since writing this section, an extension of the work has been made (ref. [31]), which is commented upon on p. 297.

ignition and therefore "knocking." "Knocking" was viewed as auto-ignition of part of the charge. The life of the droplets formed by combustion was considered to be favoured by compression of the charge, and the "dope" concentrated in these droplets diluting them and protecting them from oxidation either by means of a metallic film or by dilution. Only liquids of high critical temperature and pressure could persist as drops.

It may be true that for the pure hydrocarbon condensation occurs on compression, but in mixtures with air such as are employed in an engine the partial pressure of the vapour is much less than the saturation pressure, so that the nuclei can only remain if turbulence is insufficient and they have not had time to evaporate or are retained by particles of carbon. Engine experiments have shown that fully vaporised pentane mixtures detonate almost as readily as mixtures with a colder air intake. On the other hand, certain petrols show a larger difference for change of intake temperature, which may perhaps be due to presence of such nuclei. It has been pointed out that droplets appear to have a lower igniting temperature than the vapour, owing to the concentration of the autoxidant within them and the consequent ease with which ignition centres are set up. On the other hand, a certain amount of heat would be required to vaporise the droplets prior to ignition.

The theory, however, takes no account of the chemical behaviour of antiknock compounds, and more is required of an antiknock than protection and dilution of a droplet. The following experimental observations were made which bear on the point:—

(*a*) Kerosene ignited at 310° in the pot, petrol at 440°. The less volatile constituents of paraffin added to petrol, therefore, ought to have lowered the igniting temperature. However, 5 per cent. of kerosene raised the igniting temperature 10°.

(*b*) The critical temperature of diphenyl methane (497°) is much higher than that of petrol, so that it should act as an antiknock on the above theory. As far as igniting temperature determines detonation characteristics, this substance had no effect.

(*c*) As pentane has a higher igniting temperature than petrol and is more volatile, a small amount of petrol added to pentane should lower its igniting temperature, if the petrol concentrated in the droplets and ignition occurs at a disappearing droplet. Pentane +1 per cent. petrol had the same igniting temperature as pentane alone, while 5 per cent. petrol lowered it less than 10°.

(*d*) Dimethylaniline has a lower igniting temperature than pentane, yet 4 per cent. added to pentane raised the igniting temperature 10°.

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[21] Callendar, *Engineering*, 1927, **123**, 147 *et seq.*

These and other experiments indicate that the theory does not explain the specific action of antiknock compounds. The persistence of droplets might, however, be introduced as a secondary effect and would help to explain some of the engine results—e.g., enhanced detonation with cold air inlet.

(2) *Pyrophoric Multiple Ignition.*—Church, Mack and Boord[23] have suggested that the metallic antiknocks decompose pyrophorically, and by setting up multiple ignition centres combustion occurs more regularly throughout the charge. In criticism of this theory, in the first place, our experiments are not in agreement with the pyrophoric decomposition of such compounds; secondly, such decomposition would occur during the compression stroke and would cause pre-ignition; and thirdly, the rate of rise of temperature during explosion would be more rapid and would favour rather than disfavour detonation.

(3) *Positive Catalysts.*—Some have supposed antiknocks accelerate oxidation prior to ignition and weaken the mixture so that it will not detonate, but they retard oxidation so that this explanation is contrary to fact.

(4) *Activity of walls and other effects.*—It has been thought that the sharp points and irregularities on the surface of the interior of a cylinder promote ignition, and that if these become coated with a metal like lead that their effect is diminished. If so, then the effect should continue for a time on replacing ordinary fuel for fuel containing antiknock, but that is contrary to experience. Many other facts cited in this paper are against such an explanation. It has also been suggested that oxide or metal clouds or even carbon particles absorb the charge and fix the ions, and so weaken it that detonation is prevented. Such an explanation seems to be the opposite of Callendar's theory, and is not supported by his results or by the experiments described in these papers.

(5) *Ionisation and Radiation.*—It was supposed that charged metal atoms produced by dissociation of the antiknock collected electrons which otherwise stimulated combustion. The experiments of Wendt and Grimm[23] and of Clark and Thee[24] on this point are discussed by Garner and Saunders,[25] who have contributed further work on the subject. The only positive evidence of any effect of lead tetraethyl on ionisation in an explosion front is that provided by Garner and Saunders,[25] but under circumstances

[23] Church, Mack and Boord, *Ind. Eng. Chem.*, 1926, **18**, 534.
[23] Wendt and Grimm, *Ind. Eng. Chem.*, 1924, **16**, 890.
[24] Clark and Thee, *Ind. Eng. Chem.*, 1925, **17**, 1219. Clark, Brugman and Thee, *Ind. Eng. Chem.*, 1925, **17**, 1226.
[25] Garner and Saunders, *Trans. Faraday Soc.*, 1926, **22**, 267.

in which it would have had no effect on velocity of propagation of combustion.

Our own experiments on change of ionisation in the igniting chamber with and without antiknock did not lead to any large change being observed over and above that of thermal effects due to the lower rate of oxidation below the igniting temperature produced by the antiknock. The experiments were, however, of only a preliminary nature.

(6) *Modified Nuclear Drop Theory.*—The description of our work on the subject of antiknocks, and our own views derived as a result, were as given in the preceding pages when a second communication by Prof. Callendar from the Air Ministry Laboratory was brought to our notice.[21] In view of the similarity of the line of work, it seems advisable to refer briefly to this Paper as an addendum to this communication.*

The authors were led to look for differences between various fuels in respect of detonation in the study of the chemical reactions which were likely to occur at temperatures existing during compression before the ignition point was reached. This thesis is the same as that to which our work had led, and the conclusions that accumulation of peroxides promotes detonation, and the prevention of such accumulation by metallic dopes are so close to the views here put forward that it is of interest to point out where conclusions are not exactly in accord. We may say at the outset that the experiments add a great deal of valuable evidence in connection with the above thesis and conclusions.

The points of view which are somewhat different appear to be :—

(*a*) That the explosion of the nuclear drop is alone responsible for knocking.

(*b*) That peroxides accumulate in the drops and themselves explode, so acting as a primer causing simultaneous ignition of the drops.

(*c*) That the metallic antiknocks reduce the peroxides as fast as they are formed.

(*d*) That certain fuels (benzene, alcohol, etc.) may be placed in a class apart as non-detonating fuels.

On the first point (*a*) we agree that the liquid phase is favourable to the type of oxidation which we have discussed, and that therefore in the neighbourhood of evaporating droplets ignition centres are most likely to arise, but we do not agree that the presence of such droplets, or even nuclei, are essential to the phenomenon

* Moureu Dufraisse and Chaux [24] have put forward views to those of Callendar.

[24] Moureu Dufraisse and Chaux. C.R., 1927, **184**, 29.

known as "knocking." Knocking can occur in completely gaseous fuels (though undoubtedly it would occur at higher compression ratios if no liquid drops of the fuel were present). Engine experiments (with acetylene, pentane, etc.) have shown this, and also experiments in the ignition pot with completely vapourised fuels, and the effect thereon of antiknocks also completely vapourised. The ideas expressed as to the recondensation of vapours on the evaporating droplets as the pressure increases during the compression stroke seem to be based on the diagram of the behaviour of the pure liquid and assume more quiescent conditions than are likely in the engine cylinder. On the other hand, there is evidence for the persistence of small droplets under conditions when rapid disappearance might be expected,* so that it is likely enough that liquid droplets are present in the charge of petrol fuel, which would of course under such conditions exert an influence on the knocking characteristics of the charge.

Experiments on mixed fuels and the effect of air inlet temperature on doped fuels can be explained in terms of the presence of droplets.

The second point (*b*) is considerably divergent from the view which we have put forward; the peroxides are acting as catalysts of the combustion process in our case, and it is the general acceleration of combustion produced by the catalysts that is our view of the nature of the process, not the actual explosion of the accumulated peroxide. On Prof. Callendar's theory it is not explained why aldehydes accumulating in the drops do not promote knocking; for they have low temperatures of initial combustion and readily give rise to peroxides.

Referring to point (*c*), if antiknock action was purely a question of reduction of peroxides, then any reducing agent should act as an antiknock; this is known not to be the case. The views put forward do not seem to provide a theory of the specific action of various antiknocks.

Fourthly (*d*), there seems little justification to put other fuels in a class apart from those which detonate more readily. The whole problem is connected with the processes of slow combustion and the behaviour of all classes of fuels—even benzene and alcohol—although they may be more stable and resist oxidation must also be considered in a consistent theory. Benzene is stated to detonate at a compression ratio 8/1, and under such conditions the "activating excess temperature" would be −180°; there would appear to be no particular reason why it should detonate.

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* Gudris and Kulikowa.[27]

[27] Gudris and Kulikowa, *Z. physikal Chem.*, 1924, **25**, 121.

Apart from these considerations, the paper from the Air Ministry Laboratory is rich in experimental work and lends support in many directions to views expressed in this Paper.

4.—Summary.

A Theory of Combustion through Autoxidation, and of Antiknock action is developed.

1. The main facts regarding antiknocks are summarised.
2. Antiknocks are regarded as negative catalysts which react with and remove those substances which autocatalyse combustion.
3. In the early stages of combustion peroxides are formed which act as autocatalysts. The importance of this in connection with the establishment of ignition centres is discussed.
4. Metallic antiknocks form comparatively stable peroxides which react with and destroy the fuel peroxides and which are then regenerated.
5. The importance of the relative stability of the various peroxides and of concentration of fuel and oxygen is demonstrated.
6. The organic antiknocks are shown to exhibit similar behaviour, but themselves undergo combustion.
7. It is shown how the slowing down of the initial processes of combustion by antiknocks leads to rise in "igniting temperature" and to prevention of "knocking."
8. Other theories of antiknock action are mentioned and briefly discussed.

On Anti-Knock Dopes.*

By Dr. R. A. Weerman.†

Statement by the Laboratory of the Bataafsche Petroleum Maatschappij, of Amsterdam.

Th. Midgley's important discovery to the effect that small quantities of certain compounds dissolved in benzine have considerable influence on the detonation of a motor, led us some years ago to study several anti-knock dopes.

Three species of anti-knock dopes may be distinguished, viz. :—

1. Compounds, such as tetra ethyl lead and iron carbonyl, which, even in quantities from 0·1 to 0·2 per cent., have an anti-knock effect.

2. Compounds, such as aniline and diphenylamine, about 3 per cent. of which must be added to the petrol.

3. Compounds, such as benzene, toluene, alcohols, several tens of percentages of which must be admixed to bring about an anti-knock effect.

Our chief study was devoted to the first two classes of compounds, it being our object to get an insight into their action.

The first thing to do, therefore, was to endeavour to construct an apparatus recording the behaviour of simple petrol and that of petrol mixed with an anti-knock dope. If a property could be found in which two such petrols (chemically varying only in a few hundredths of a fraction of metal) *greatly* differed in their blending with air, then the same cause would in all probability be found to underlie this difference as their different behaviour in the motor cylinder.

To explain the knocking of an engine, Midgley[1] evolved the high velocity, high pressure wave theory ; the spontaneous ignition temperature plays no part in this theory, as he is of opinion that a very small quantity of a substance, such as a metal dope, cannot affect it.

Ormandy and Craven[2] examined the effect of anti-knock agents upon the spontaneous ignition temperature in Moore's spontaneous ignition apparatus. They, however, found 14° decrease for 0·25 gr. of Pb $(C_2H_5)_4$ in 100 c.c. of heptane in a current of oxygen, and

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* These experiments were carried out in 1925 ; a statement based on them was not issued earlier for various reasons.

† Paper received April 1st, 1927.

[1] *Ind. Eng. Chem.*, 1922, **14**, 894.

[2] *J. Inst. Petr. Techn.*, 1924, **10**, 335.

4° increase for amyl nitrate and nitrite which, according to Midgley are pro-knock; the very contrary, therefore, of what was to be expected. They found 14° increase for 1 gr. of p-toluidine in 100 c.c. of heptane. They came to the conclusion that "The foregoing results show that the addition of anti-detonating agents does not affect the ignition temperature to anything like the extent of their effect in an engine."

Ricardo[3] states: "As regards detonation, undoubtedly the most important recent work is that of Midgley on the effect of the organo-metal compounds. . . . No explanation or beginnings of an explanation appear yet to have been found as to the precise behaviour of these organic compounds, which, unlike the aromatic compounds, appear to have no influence whatever either upon the rate of flame propagation or upon the self-ignition temperature of the fuel."

Although, therefore, with a view to the foregoing, experiments with self-ignition temperatures were not very promising, we nevertheless considered it useful to test petrols, with and without anti-knock dope, under identical conditions for their S.I.T.

We must premise that the S.I.T. of a substance is a relative conception; record of it is only valuable if accompanied by accurate details of the conditions under which the test was carried out.

We made various apparatus for the determination of the S.I.T., but the iron instrument represented in Fig. 1 suited us best.

Our experiments had the surprising result that we found that, contrary to current opinion (the tests were carried out in the beginning of 1925), there certainly is *a very great difference between the self-ignition temperature of a petrol with and without anti-knock dope.*

Method of Determination.

Clean the crucible (Fig. 1) carefully with fine emery paper; this may best be done by placing it on a lathe for a moment and then blowing it out. Heating is done electrically, and is so regulated with the help of a variable rheostat that the temperature increases by 5° to the utmost, in 2 minutes. Let one drop fall into the instrument every 10° and, in the neighbourhood of the temperature at which ignition is expected, every 5°; first, always let several drops fall on a watch glass so as to be certain that none of the falling drop first evaporates. The drop should fall precisely in the centre; in our tests the size of the drop amounted to 0·013 c.c.

[3] The Institution of Automobile Engineers. Report of the Motor Fuels Committee, Vol. XVIII., Part I. p. 327.

in the case of Shell petrol. The air supply must be absolutely regular; in our apparatus it amounted to 330 c.c. per minute.

There is no object in determining the S.I.T. in this apparatus to within an accuracy of one degree; the method is not so precise

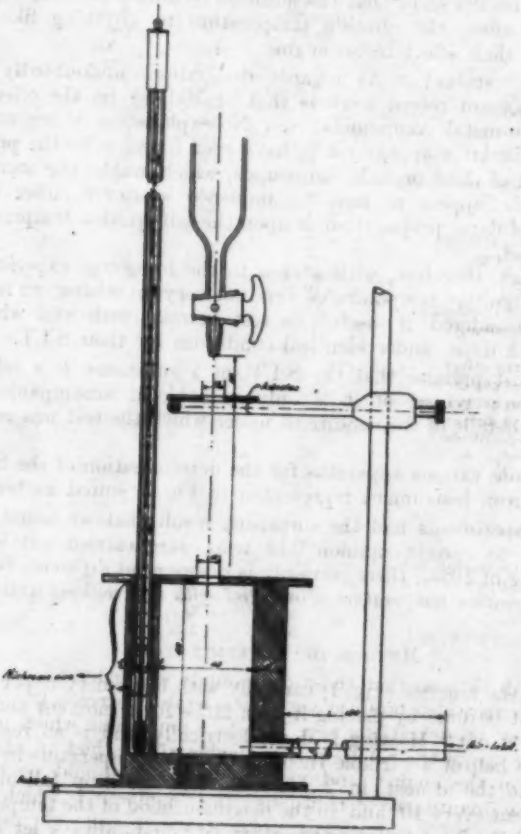


FIG. 1.

and there is, therefore, no correction for emergent thermometer stem.

In every determination of the S.I.T. of a petrol with an anti-knock dope the blank determination must be carried out first;

if this differs from a previous determination, the crucible must first be cleaned.

We tested a great many compounds of 22 elements. In the following table we give the results of some of these.

	Gram per litre.	S.I.T.	S.I.T. petrol.	Difference.
Tetra ethyl lead	0·5	440	335	105
	1	465	335	130
Iron carbonyl	2·9	505	335	170
Nickel carbonyl	1	395	335	60
Mercury diethyl	2	340	335	5
Selenic diethyl	0·5	450	335	115
	1	475	335	140
Diethyl tellurium	1	390	335	55
	2	405	335	70
Boric triethyl	4	325	335	—10
Chromium carbonyl	4	415	335	80
Tetra ethyl tin	2	410	335	75
	4	445	335	110
Zinc diethyl	10	325	335	—10
Aluminium triethyl	2	325	335	—10
Bismuth triphenyl	1	420	335	85
	2	440	335	105
Silicon tetra ethyl	4	325	335	—10
Cobalt acetylacetone	2	335	335	0
Manganese acetyl acetone	2	335	335	0
Iron acetyl acetone	2	335	335	0
Ethyl mercaptane	2	335	335	0
Diethyl sulphide	2	335	335	0
Ethyl iodide	10	395	335	60
Aniline	5	400	335	65
	10	415	335	80
Diphenylamine	5	410	335	75
	10	425	335	90
Acetyl diphenylamine	5	335	335	0
p-Phenitidine	5	400	335	65
	10	440	335	105
Pyramidon	5	345	335	10
Dimethyl 3-5 pyrazol	5	335	335	0

It will be seen that those compounds which have a good anti-knock effect also produce very considerable increase in the S.I.T.

So far, no deviations were found. Compounds which produced an increase in the S.I.T. in the crucible always had an anti-knock effect in the engine, and vice versa. Care should be taken in drawing quantitative conclusions. Two compounds which produce the same S.I.T. in certain concentrations will not necessarily produce precisely the same H.U.C. in the engine; for that the conditions obtaining in the crucible and the motor cylinder are too dissimilar.

It appears that only those elements are active which produce oxides which can be reduced under the circumstances prevailing in the engine during the compression stroke, or appear in various

degrees of oxidation. Furthermore, it is very important that the compound should be volatile, so that it is homogeneously distributed in the cylinder.

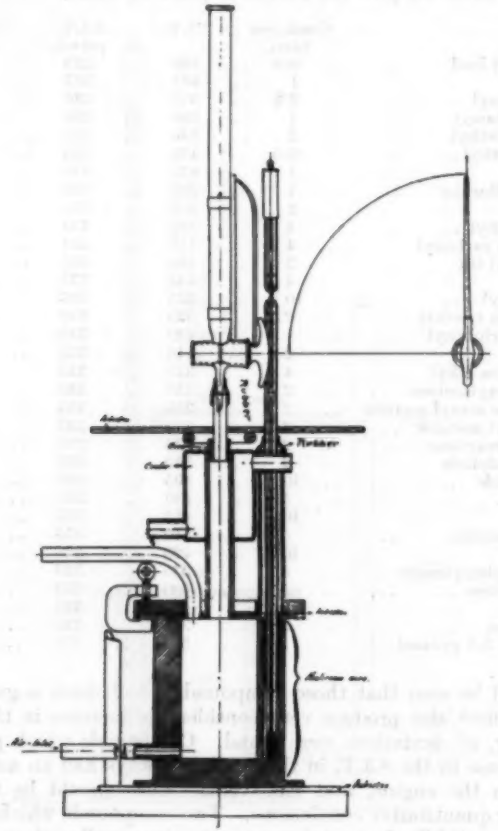


FIG. 2.

Although Si $(C_2H_5)_4$ is described in the I.G. Farbenindustrie's German Patent No. 427,276 as an anti-knock agent, according to the foregoing theory, this could not be so. As a matter of fact, we found a decrease in the S.I.T., and it also produced a slight decrease in the H.U.C. in Ricardo's variable compression engine.

It is interesting to note that, with diphenylamine, the augmenting effect on the S.I.T. disappears when the hydrogen atom attached to the nitrogen is substituted by the acetyl group.

To facilitate a closer study of the action of the metal dopes, the crucible was arranged in the manner shown in Fig. 2. The outgoing gas mixture was conducted through U-tubes, which were cooled with solid carbon dioxide and alcohol.

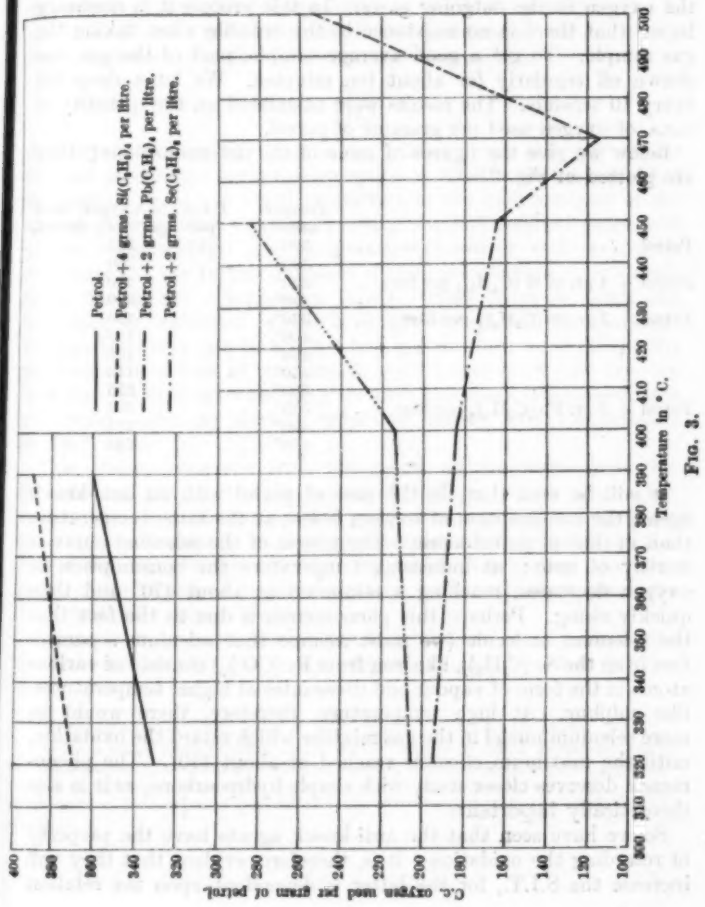

Petrol.
Petrol + 6 grms. $Si(C_2H_5)_4$ per litre.
Petrol + 2 grms. $Pb(C_2H_5)_4$ per litre.
Petrol + 2 grms. $Se(C_2H_5)_2$ per litre.
Temperature in ° C.
c.c. oxygen used per gram of petrol.

FIG. 3.

In a test at 320° (in this altered apparatus, the S.I.T. of the petrol used was 410°) with petrol only and with petrol+2 gr. of Pb $(C_2H_5)_4$ per litre (one drop every 30 seconds) it transpired that less water was formed and the acid number of the aqueous as well as of the oil layer was lower for the petrol with Pb $(C_2H_5)_4$ than for petrol without a dope.

When it became apparent that the addition of Pb $(C_2H_5)_4$ retarded the speed of oxidation to such an extent, we proceeded to determine the oxygen in the outgoing gases. In this process it is necessary to see that there is no resistance in the crucible when taking the gas sample. To get a good average sample, part of the gas was drawn off regularly for about ten minutes. We let a drop fall every 10 seconds. The results were calculated on the quantity of c.c.s. of oxygen used per gramme of petrol.

Below we give the figures of some of the determinations; they are plotted in Fig. 3.

	Temperature.	C.C.s of oxygen used per gr. of petrol.
Petrol	320° ..	330
	390° ..	360
Petrol + 4 gr. of Si $(C_2H_5)_4$ per litre ..	320° ..	370
	390° ..	390
Petrol + 2 gr. Se $(C_2H_5)_2$ per litre ..	320° ..	195
	400° ..	185
	450° ..	165
	470° ..	115
	500° ..	255
Petrol + 2 gr. Pb $(C_2H_5)_4$ per litre ..	320° ..	205
	400° ..	215
	450° ..	285

It will be seen that, in the case of petrol with an anti-knock agent, the consumption of oxygen is less at the same temperature than in that of petrol alone. The course of the selenium curve is worthy of note; at increasing temperature the consumption of oxygen decreases, reaching a minimum at about 470° and then quickly rising. Perhaps this phenomenon is due to the fact that the selenium molecule (we must assume that selenium separates first from the Se $(C_2H_5)_2$, like iron from Fe $(CO)_5$) consists of various atoms in the form of vapour and dissociates at higher temperatures, like sulphur. At high temperature, therefore, there would be more selenium nuclei in the gas mixture which retard the oxidation, until the maximum effect is reached at about 470°. The phenomenon deserves closer study with simple hydrocarbons, as it is also theoretically important.

So we have seen that the anti-knock agents have the property of retarding the oxidation; it is, therefore, evident that they will increase the S.I.T., for the latter is dependent upon the relation

between the speed with which the heat is developed and with which it escapes.

Several theories have been drawn up [4] on the detonation of the gas mixture in the motor cylinder and on the action of anti-knock agents. In my opinion, in observing the phenomena of combustion in the engine, the error is usually committed of concentrating too much on what happens after the gas mixture is ignited by the spark. The benzine-air mixture is regarded as an indifferent gas mixture during the compression, to which the gas laws may be applied. For the calculation of the temperature at the end of the compression stroke, the following equation is used :—

$$Te = Ta \left(\frac{Pe}{Pa}\right)^{\frac{n-1}{n}}$$

Actually, however, the case is as follows: At the end of the exhaust stroke the compression space is filled with the very hot combustion gases. A small proportion of the hydrocarbons of the incoming air-benzine mixture, meeting the hot residual gases, will oxidise considerably. The temperature, however, will soon drop on account of the further infusion of the cold mixture, only to rise again during the compression stroke. Here there is again the beginning of oxidation which is finally completed by sparking. The gas laws may not be applied to a gas mixture in reaction. To ascertain the action of anti-knock agents one must not try—or only try—to find out what they do after the spark has passed, but also what they do during induction stroke and compression stroke [5].

This theory concords with the result of the tests made by Ricardo and Co., in Old Shoreham in 1925, in which the engine was so arranged that a special valve was opened and ignition interrupted alternately, so that gas samples could be taken at the end of the compression stroke, from which it appeared that the gases of an undoped benzine contain more oxidation products than those of a doped benzine.

I here wish to acknowledge my indebtedness to my assistant, Mr. Schumacher, for his lively support in the execution of the tests.

[4] Clark, Brugman, Thee, *Ind & Eng. Chem.* Vol. XVII. (1925), 1229.

[5] From a letter from London in the News Edition of 22nd February, 1927, of *The Journal of Industrial and Engineering Chemistry*, it appears that the British Air Ministry Research Department now approves this theory. They there assume that organic peroxides come into being during the compression stroke.

Carbon Ratio.

By Murray Stuart.*

Recently it has become noticeable in scientific literature in this country that there is a growing habit of introducing diverse interpretations of the carbon-ratio theory, and reference is occasionally made to it in such a way as to give a confusing impression of what is really meant by it. For example, in a paper recently published in this Journal the following occurs :—

"A line of research which has received considerable attention in recent years and provided some illuminating if not generally applicable results has for its object a correlation between the metamorphosis of rocks and the character of their oil contents. David White first directed attention to the relationship between the carbon-hydrogen contents of a coal and the nature of hydrocarbons in a geological succession. He demonstrated that in the Pennsylvanian Oilfields heavy oils of 0.835 to 0.875 sp. gr. were met with when the ratio of fixed C to H in coals was 50 to 55 per cent.; that oils of 0.802 to 0.825 sp. gr. were found when the ratio was between 55 to 60 per cent.: that much gas and light oil appeared in the zone of 60 to 65 ratio, and that only bituminous residues and traces of oil and gas occurred when the ratio of C to H reached 70 to 80 per cent."

In another paper, also published in this Journal within the last twelve months, the following occurs :—

"In the Appalachian geosyncline, the main coal series occurs above the oil series and the degree of metamorphism as measured by the carbon content of the coals (ash free) has been correlated with the grade of oil beneath. From a map contoured in equal "fixed carbon" lines (isovols) the oil prospects of different areas can be estimated. . . . What justification is there for assuming that the method of sampling and the stated limits have allowed for the important factors, other than regional metamorphism, which influence the C/H ratio? The occurrence of banded bituminous-anthracitic coal seams in Scotland and the detailed evidence concerning the relation of anthracite and other coals in South Wales, shows that the C/H ratio is largely influenced by the amount of preliminary biological decomposition as well as the intensity of geophysical factors. The carbon ratios of cannels are 10-20 per cent. lower than of corresponding bituminous coals."

* Paper received March 26, 1927.

In a comparatively recently published book dealing with oil technology the relationship between the carbon ratio of a coal and the prospects of finding oil in associated strata is summed up as follows:—

Ratio of C to H.	*Prospects.*
50 to 55 per cent.	best
55 ,, 60 ,, ,,	weaker.
60 ,, 65 ,, ,,	very little.
70 ,, 80 ,, ,,	nil.

In each of the three instances given above, the meaning the writers intended to convey must be obvious to those who have studied this particular subject, but to those who have not done so, the paragraphs, as worded, can only be confusing.

The recognition by David White of the frequent relationship in America between the carbon ratio of coals and the likelihood of occurrence of oil in the associated strata was one of the great advances made in oil geology in the first quarter of the present century. Since the observation was first made by David White investigation of the phenomenon has been carried out by many geologists, and at the present day the term "carbon ratio" is one of the fundamental terms of oil technology. It is obvious, therefore, that the meaning of carbon ratio should be clearly defined, and that diverse interpretations of it that have found their way into scientific or technical literature should be standardised as soon as possible.

In David White's paper "Some Relations in Origin between Coal and Petroleum," published in the Journal of the Washington Academy of Science, Vol. V., pp. 189-212, what is now known as the carbon ratio of a coal is referred to as the percentage of fixed carbon (pure coal basis) in the coal. In other words the analysis of a coal is generally expressed in terms of

Moisture,
Fixed carbon,
Volatile Matter,
Ash.

Neglecting the moisture and the ash, it is the percentage ratio of fixed carbon to volatile matter that is meant, when the carbon ratio of a coal is referred to. As the *percentage* ratio is taken as the basis of the carbon-ratio theory, it is not necessary to express the ratio as a ratio, and for convenience it is expressed simply by the percentage of fixed carbon in the sum total of the fixed carbon plus volatile matter of a coal. Thus it is at once evident when it is stated that the carbon ratio of a coal is, say, 55 that the ratio of fixed carbon to volatile matter in the coal equals 55 to 45.

If all the carbon in coal existed in the fixed carbon portion and the volatile matter consisted exclusively of hydrogen, then it might be permissible to refer to the carbon ratio as the C/H ratio, but since such is not the case, and there is a very considerable quantity of carbon in the volatile matter of a coal, it is obvious that to do so is wrong. Not only is it wrong, but it is obvious that values which apply to the carbon ratios of coals do not apply to the percentage ratios of carbon to hydrogen in the coals. For example, coals are known which have a carbon ratio of 50, but the percentage ratio of carbon to hydrogen in the same coals is over 90.

The Action of Sulphuric Acid on Unsaturated and Aromatic Hydrocarbons.

By W. R. Ormandy, D.Sc., F.I.C., F.C.S., M.I.A.E., M.I.Chem.E., and E. C. Craven, B.Sc., F.C.S. (Members).*

The determination of the aromatic content of a petroleum spirit containing olefines, being a problem which has not yet received an adequate solution it was thought of interest to inquire into the possibility of the determination of the aromatic sulphonic acids formed on shaking with 98 per cent. sulphuric. It has usually been accepted that strong sulphuric removes unsaturateds completely. Moore,[1] for example, found the bromine absorption of cracked spirit practically to vanish on shaking with acid as weak as 88 per cent. On the other hand, Brooks and Humphrey,[2] working chiefly with 85 per cent. acid state that large amounts of olefine polymers are formed. It must be pointed out, however, that these workers appeared to have relied simply on boiling points to determine the nature of the products formed. The initial ideas in the present work were somewhat as follows. On shaking the spirit under test for half-an-hour with 3 volumes of 98 per cent. sulphuric acid the aromatics and olefines should go entirely into solution, leaving a residue of open and closed chain paraffins, the loss in weight giving the total aromatics and unsaturateds. The acid wash should contain aromatic sulphonic acids and alkyl hydrogen sulphates. On dilution with water and boiling the latter should hydrolyse leaving a mixture of sulphuric acid and sulphonic acids. The barium salts of the latter could be formed by neutralisation with barium carbonate and a determination of the barium in solution would give the amount of sulphonic acids.

The results of the work have shown that the method is only sound in the absence of unsaturateds and that in the presence of the latter there are flaws in the scheme all along the line. What has been found is :—

1. That large proportions of the olefines do not dissolve in the sulphuric acid, but are thrown out as saturated hydrocarbons, probably open chain paraffins.
2. That alkyl hydrogen sulphates are only formed in small quantity from some unsaturateds.
3. That a large proportion of the aromatic sulphonic acids disappear when formed in the presence of olefines.

* Paper received February 22, 1927.

[1] Moore, *J. Inst. Petr. Techn.*, 1925, **53**, 587.

[2] Brooks and Humphrey, *J. Amer. Chem. Soc.*, 1918, 822.

The initial experiments were made in the absence of unsaturated hydrocarbons in order to test the barium method. The aromatics used consisted of a mixture of equal volumes (nearly enough equal masses) of benzene, toluene and m-xylene each of high purity. The aromatics were mixed in various proportions with saturated hydrocarbons (a straight petrol spirit exhaustively washed with 98 per cent. H_2SO_4). Fifty c.c. of the mixture were shaken for half an hour with 150 c.c. of 98 per cent. H_2SO_4. After standing all night the acid layer was run off into water and the residual spirit measured. An aliquot of the diluted acid representing 1 c.c. of the original mixed spirit was diluted to about 150 c.c. and neutralised with barium carbonate (14 gms.). The milk was boiled to expel CO_2 and then filtered, the residue being carefully washed. The barium in solution was determined by precipitation as sulphate or carbonate, usually the latter, being quicker. Check tests showed no difference in the results of these two variations.

1 gm. $BaSO_4 = 0{\cdot}918$ c.c. aromatics.
1 gm. $BaCO_3 = 1{\cdot}086$ c.c. aromatics.

The first results obtained were very irregular and mostly low. A serious source of error was found to be the impurity of the barium carbonate employed. Even when using "A. R." quality carbonate and sulphuric acid a "blank" amounting to nearly 2 per cent. of aromatics was obtained. It was immaterial if the blank were simply done on 3 c.c. of sulphuric acid, or by washing 50 c.c. of the stock saturated hydrocarbons. After a great deal of work it was discovered that consistent results could be obtained if the barium carbonate neutralisation and subsequent filtration were carried out entirely in the cold. The filtered solution had then to be boiled to drive off CO_2 and refiltered before the determination of the barium in solution. The following results were obtained by this modification:—

Aromatics taken. Per cent. vol.	Aromatics found. Per cent. vol.
Blank.	1·5 (deducted in tests under).
5	5·1, 5·2, 5·1
10	9·8, 9·8
15	14·6, 14·7
20	19·6, 19·8
25	24·9, 25·1
30	29·6, 29·7

The loss to acid in each case was about $\frac{1}{2}$ per cent. greater than the aromatics taken.

The results were found to be unaffected by boiling the diluted acids before cooling and neutralising.

The test being now in working order unsaturated hydrocarbons were introduced. These were:—

(*a*) Fraction of Kahlbaum amylene .. .. 35–38° C.
(*b*) Fraction of turpentine .. .. .. 155–163° C.

The latter is, no doubt, largely pinenes which may be considered as cyclic olefines.

The following table gives results obtained with turpentine:—

Aromatics taken. Per cent. vol.	Turps. taken. Per cent. vol.	Aromatics found. Per cent. vol.	Loss to acid. Per cent. vol.
0	10	0·2	10·6
0	20	0·1	20·6
0	100	2·6	90·0
5	20	4·0	24·6
10	20	9·8	29·4
20	20	18·7	39·2

The low aromatic results obtained in the presence of 20 per cent. turpentine led to various experiments being tried, such as successive washing with fresh acid, weighing out aliquots of the whole wash acid and so on, but the results were from 17—19 per cent.

The following table gives some results with Amylene:—

Aromatics taken. Per cent. vol.	Amylene taken. Per cent. vol.	Aromatics found. Per cent. vol.	Loss to acid. Per cent. vol.
0	100	1·2	50·0
15	20	12·4	25·8
20	10	18·3	26·0

Here it appears more clearly that the acid loss is not equal to the sum of the aromatics and unsaturateds, only about 50 per cent. of the latter appearing to dissolve, and that the aromatics found are low. This led to further experiments being made with acid and amylene alone, the results of which will be given a little further on.

At this point of the work a new supply of barium carbonate of A.R. quality was obtained. Since the previous lots had been in a granular form necessitating very tedious grinding in a mortar in order that the cold neutralisation should not take an unduly long time, the new supply was delivered already moderately finely ground. Whether due to the extra handling this entailed or not unfortunately the blank test on this carbonate was very high and very uncertain, giving any result from 3 per cent. aromatics downwards.

It was decided that since small amounts of water-soluble salts would be present in any barium carbonate obtainable, that it would be better to rely on the conductivity of the final liquor as a measure of the sulphonate present and to make the method empirical.

The following scheme was adopted. 10 c.c. of the mixture under test was shaken with 30 c.c. H_2SO_4 allowed to stand a short time and the acid run off into water, the residual spirit being then washed with water. The diluted acid and washings were made

to 250 c.c., 25 c.c.s of this solution representing 1 c.c. of original spirit were added to a milk of 14 gms. $BaCO_3$ in 100 c.c. of water and raised slowly to boiling. The neutral mixture was cooled, and diluted to 250 c.c. with boiled-out distilled water. The solution was filtered off rejecting the first portions and its conductivity determined in a quartz U-tube fitted with electrodes of platinised nickel. An ordinary P.O. box bridge was used with low-resistance telephones and current from a valve oscillator, the frequency being 3400. It was found that results to 0·1 per cent. of aromatics were easily obtained so that it was not thought worth while using a more elaborate bridge. The calibration in the absence of unsaturateds was as follows:—

Per cent. aromatics taken.	Resistance ohms, 15° C.	Conductivity. Arbitrary units.
0 (blank)	101,000	99
5	31,300	313
10	18,950	528
15	13,450	744
20	10,400	961

The figures plotted give practically a straight line.

Experiments were made using all combinations of 0, 5, 10 and 20 per cent. aromatics with 5, 10 and 20 per cent. of amylene or turpentine.

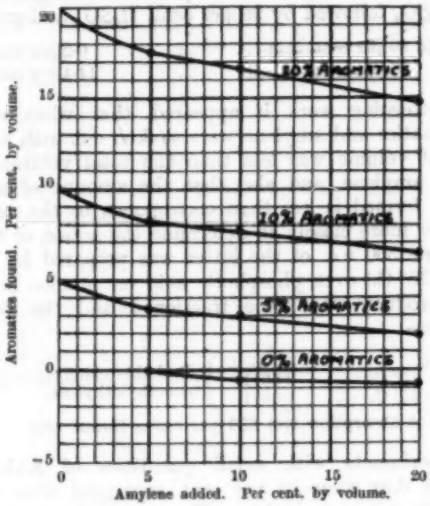
Amylene.

Aromatics. Per cent. vol.	Amylene. Per cent. vol.	Resistance ohms, 15° C.	= Aromatics. Per cent. vol.
0	5	100,000	Nil
0	10	125,000	0·5
0	20	140,000	0·7
5	5	40,100	3·5
5	10	43,300	3·1
5	20	50,500	2·0
10	5	21,900	8·3
10	10	23,300	7·7
10	20	26,500	6·5
20	5	11,700	17·6
20	10	12,300	16·6
20	20	13,600	14·8

Turpentine.

Aromatics. Per cent. vol.	Turpentine. Per cent. vol.	Resistance ohms, 15° C.	= Aromatics. Per cent. vol.
0	5	74,000	0·8
0	10	96,000	0·1
0	15	100,000	Nil
0	20	100,000	Nil
5	5	34,700	4·7
5	10	36,900	4·0
5	20	40,700	3·4
10	5	20,800	8·8
10	10	21,500	8·5
10	20	21,700	8·4
20	5	11,200	18·4
20	10	11,300	18·2
20	20	11,600	17·8

These results are shown in the graphs.



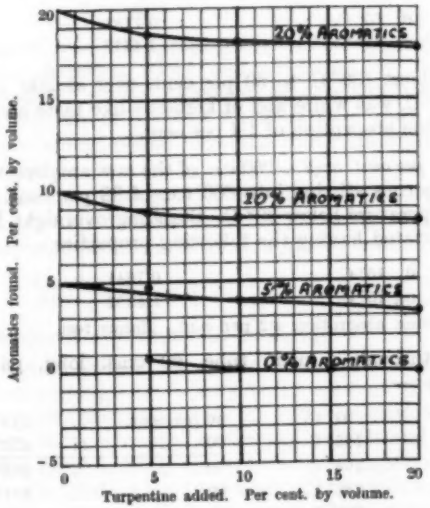


FIG. 1.

A further experiment was made in which a mixture containing 20 per cent. aromatics, 20 per cent. amylene, was shaken out with 80 per cent. H_2SO_4 followed by 98 per cent. H_2SO_4 and gave :—

Aromatics in 80 per cent. acid	0·2 per cent.
„ 98 per cent. „	14·4 per cent.

From the foregoing work it appeared that when mixtures containing aromatics and amylene were shaken out with sulphuric acid the loss of volume was less than the total volume of the aromatics plus amylene, and also that the amount of aromatic sulphonic acids formed is less than corresponds to the aromatics taken. In order more closely to determine the action of the acid on amylene some 300 c.c. of the latter was prepared by passing fusel oil (125–135° C.) over phosphoric acid on pumice heated to 400° C. The product was twice fractioned and the following fraction taken :—

B.p. ..	33–37° C.	Probably chiefly trimethylethylene.
d 15° C. ..	0·6611	
n_D 15° C. ..	1·3871	

Bromine absorption test 233 per cent., Hanus test.

Previous experiments with small quantities of Kahlbaum's amylene showed that some 55 per cent. separated after shaking with 3 vols. of 98 per cent. H_2SO_4. The separated oil showed :—

d 15° C.	0·7727
n_D 15° C.	1·4319

Distilled from about 130° C. to 60 per cent. over at 260° C. The distillate to 260° C. was white and of kerosene-like taste and odour and had a bromine absorption of 1·4 per cent.

Amylene in 98 per cent. acid.—200 c.c. of the new amylene was run slowly under vigorous stirring into 600 c.c. of 98 per cent. H_2SO_4 keeping the temperature below 20° C. Standing overnight 120 c.c. of top layer separated having the following properties :—

d 15° C.	0·7641
n_D 15° C.	1·4362

Bromine absorption 4·2 per cent., Hanus test.

Fractionated through a plain tube, 60 cms. long, gave the following figures :—

Drop	91° C.	50 per cent. ..	215° C.
10 per cent. ..	145° C.	60 „ ..	232° C.
20 „ ..	163° C.	70 „ ..	263° C.
30 „ ..	180° C.	80 „ ..	301° C.
40 „ ..	198° C.	90 „ ..	353° C.

The distillation above 232° C. was carried on in an Engler flask. The following fractions were collected and examined.

No.	° C.	Bromine absorption. Per cent.	d 15° C.	n_D 15° C.	r_L.
1	To 163	0·2	0·7194	1·4078	0·3428
2	„ 198	0·3	0·7467	1·4203	0·3391
3	„ 232	0·6	0·7679	1·4350	0·3398
4	„ 301	4·1	0·7925	1·4471	0·3372
5	Residue	9·6	0·8207	1·4616	0·3347

The column headed r_L is the specific refractivity calculated from the Lorenz-Lorentz formula :—

$$r_L = \frac{n^2 - 1}{(n^2+2)d}$$

In the graph (Fig. 2) the theoretical curves of the specific refractivities against molecular weights are given for paraffins, naphthenes and unsaturateds. These are calculated from the following values for the molecular refractions :—

C	= 2·418
H	= 1·100
Double bond	= 1·733

Giving

Paraffins	r_L	= 0·3299+1·54/M
Naphthenes	r_L	= 0·3299
Unsaturateds	r_L	= 0·3299+2·39/M

The upper scale of the graph gives the boiling points of the normal open-chain paraffins. The boiling points of naphthenes and unsaturateds of similar molecular weights will not differ greatly. The refractivities of the five fractions have been plotted against their mean boiling points since the mean molecular weights were not determined.

The specific refractivities of the fractions point clearly to their being chiefly open-chain paraffins. This is confirmed by an elementary analysis of the original top layer before fractionation :—

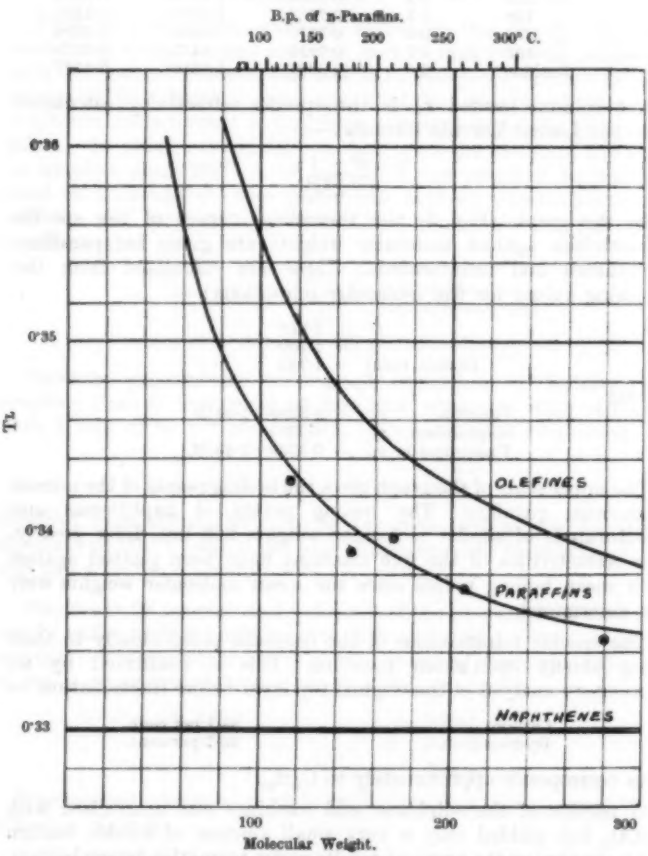
Carbon	84·1 per cent.
Hydrogen	15·7 per cent.

This corresponds approximately to C_9H_{20}.

A portion of the sulphuric acid washings was neutralised with $BaCO_3$ but yielded only a very small amount of soluble barium salts, confirming the previous results under aromatics determination. The barium salts, converted to the sodium salts and extracted with hot alcohol gave a small amount of very imperfectly crystalline material. On diluting the remainder of the wash acid with 3 vols. of water some 40 c.c. of oil separated. This steam distilled gave

12 c.c.s of oil, much heavy oil being left in flask. The distilled oil showed :—

d 15° C. 0·8606 } r_L = 0·3384
n_D 15° C. 1·4943 }
Bromine absorption .. 251 per cent. (Hanus)
Molecular weight .. 210



SPECIFIC REFRACTIVITY OF FRACTIONS FROM ACID-TREATED AMYLENE.

FIG. 2.

On distillation from a small flask :—

10 per cent. over at 190° C. 90 per cent. over at 260° C.

The bromine absorption and molecular weight point to this oil being a mixture of triolefines.

Calculated for $C_{18}H_{34}$, $r_L = 0{\cdot}340$

Amylene in 80 per cent. acid.—Earlier experiments with Kahlbaum's amylene showed that some 75 per cent. separates after shaking with 3 vols. of 80 per cent. sulphuric acid.

Twenty-two c.c.s of the new amylene shaken with 3 vols. of 80 per cent. acid gave 18 c.c. of separated oil :—

d 15° C. 0·7715
n_D 15° C. 1·4388 } $r_L = 0{\cdot}3408$
Bromine absorption 18·5 per cent.

It would appear that the conversion to saturated open-chain paraffins is not quite so complete as with the stronger acid.

Amylene plus Benzene in 98 per cent. acid.—A mixture of 100 c.c. benzene with 100 c.c. amylene was run slowly under stirring and cooling as before into 600 c.c.s of 98 per cent. acid. Volume of separated oil 43·5 c.c. :—

d 15° C. 0·8001
n_D 15° C. 1·4750 } $r_L = 0{\cdot}3519$
Bromine absorption .. 1·8 per cent.

An Engler distillation showed a smooth distillation range from 127° C. to 76 per cent. over at 357° C.

The high density and specific refractivity indicate that phenyl groups have gone into the separated hydrocarbons. Further shaking with 98 per cent. acid, however, failed to dissolve anything further. The low results for aromatics in the presence of unsaturateds appear to be explained by this phenylation of the separated hydrocarbons.

Petroleum fractions in 98 per cent. acid.—Crude cracked spirit was fractionated through a 60 cm. tube until 400 c.c. of each of the following fractions had been collected :—

I.	20– 40° C.
II.	40– 70° C.
III.	70–100° C.
IV.	100–130° C.
V.	130–160° C.

Each fraction was run slowly into 400 c.c. of 98 per cent. acid under stirring and cooling. After standing and separating the top layers were distilled through the same still head. No definite cutting point could be perceived so that cuts were made about 30° C. above the nominal end point of the fraction in question.

It must be remembered that even if sulphuric acid simply removed aromatics and unsaturateds the end point of the residue would be raised on account of the removal of binary mixture components.

The residues from fractions III., IV. and V. were dark in colour, so were rewashed with a small amount each of strong acid which

brought them white without affecting their volume appreciably. Very little SO_2 was produced in the distillations.

The residues showed the following figures:—

Fraction.	Vol. c.c.	Br. No. Per cent.	d 15° C.	n_D 15° C.	r_L
I. ..	143	4·3	0·7563	1·4251	0·3381
II. ..	127	4·2	0·7732	1·4329	0·3361
III. ..	96	3·9	0·8137	1·4518	0·3314
IV. ..	52	2·7	0·8362	1·4620	0·3287
V. ..	27	2·2	0·8701	1·4814	0·3273

The boiling ranges from an Engler flask were as follows:—

	I. °C.	II. °C.	III. °C.	IV. °C.	V. °C.
Drop B.	92	117	144	158	178
20 per cent. over ..	134	148	185	188	271
40 „ „ ..	164	176	216	247	292
60 „ „ ..	198	212	250	265	313
80 „ „ ..	258	268	298	310	350(about)
90 „ „ ..	318	309	337	—	—

The first three fractions are thus undoubtedly open-chain paraffins of boiling-point range similar to the products from amylene. The two heaviest fractions have specific refractivities of the naphthenic order but it is probable that these two fractions may contain a little oxygen or sulphur which would reduce the refractivity. Their amounts were too small to enable an extended examination to be made.

Conclusions.

1. In the absence of olefines, aromatics can be determined by the amount of their sulphonic acids formed on shaking with 98 per cent. sulphuric acid.

2. Amylene and heavier olefines occurring in cracked spirit when shaken with sulphuric acid yield large proportions of saturated hydrocarbons of higher boiling point and not olefine polymers as has hitherto been assumed.

3. These saturated hydrocarbons are probably open-chain paraffins.

4. In the presence of olefines, aromatics are not entirely removed by sulphuric acid but partly condense with the hydrocarbons from the olefines.

5. The sulphuric acid wash from amylene contains very little amyl hydrogen sulphate.

The authors desire to acknowledge the financial assistance received from the Distillers Company, Ltd., and the Fuel Research Division of the Department of Scientific and Industrial Research towards the expenses of this research.

Pliocene Oil Seepages in Persia.

By G. M. Lees, M.C., D.F.C., F.R.G.S., F.G.S. (Associate Member).*

The historical antiquity of Persian oil and gas seepages is well known. Biblical references, legends of the Fire Worshippers, the accounts by Herodotus of the exploitation of oil in Susiana (Qirab N. of Dizful) and by Plutarch at Ecbatana (Hamadan) are frequently quoted as a prelude to an estimation of future potentialities. It may, therefore, be of interest to place on record the geological antiquity of Persian seepages, but it is hoped that future estimates of potentialities will not be unduly expanded in proportion.

The intensive orogenetic phase of South Western Persia is of late Pliocene age, but preliminary gentle folding movements commenced considerably earlier. During the Miocene period when the Fars series was being deposited very gentle folding was already taking place, and at the commencement of the Pliocene these movements were considerably accelerated. Rapid erosion took place in the anticlinal regions, and a series of conglomerates, sands and clays was deposited in the broad synclinal valleys. These deposits, termed the Bakhtiari series, have been divided into an upper and lower group, separated by a marked discordance, but in the absence of fossil evidence exact correlation throughout the country is impossible. The lower group overlies the Upper Fars conformably, or in places the two series are separated by an angular discordance, the division, in the former case, being purely arbitrary. The series attains a thickness of about 15,000 feet in one area.

Oil, apparently indigenous, occurs at various horizons throughout the Middle and Lower Fars and exceptionally in Upper Fars, although commercial production is obtained principally from the Lower Miocene (Asmari) limestone. When these petroliferous horizons were first exposed by erosion in the anticlinal regions considerable seepages resulted, striking testimony of the prolificacy of which is afforded by large deposits of derived bitumen pebbles or bituminous sands occurring in the Bakhtiari beds in different parts of the country.

The most extensive deposits of such secondary bitumen occur at various places between Tang-i-Tikab and Tashan, on the south-east flank of the Kuh-i-Khaiz anticline (N.E. of Behbehan plain.) The Pliocene oil seepages were supplied from a strongly petroliferous zone in the Lower Fars Gypsum series and thick inspissated oil,

* Paper received February 18, 1927.

boulders and grains of bitumen were deposited in the valley together with the normal Bakhtiari sandstones and conglomerates. These beds transgress in places on to the Lower Fars, with which they

have subsequently been strongly infolded. At Tashan at the N.W. end of Kuh-i-Khaiz, the bitumen becomes liquid during the hot summer months, and is exploited locally by digging shallow pits into which the bitumen slowly oozes. It occurs either as the cementing material of sandstones, as small rounded grains in sands, or as boulders in conglomerates.

Between the rivers Rud-i-Ala and Rud-i-Zard, about 10 miles north of Mamatain, deposits of detrital bitumen have been found at several places in similar circumstances. The greatest development and best exposures are at Chalgah. Other similar deposits have been found on the north-east flank of Kuh-i-Asmari, so it is highly probable that this mountain has been the site of oil seepages uninterruptedly from Pliocene to the present day.

A unique occurrence was examined by the writer this year at a place called Khadda Sur, between Kuh-i-Asmari and Malamir. The bitumen occurs as cementing material in a conglomerate bed in Lower Bakhtiari which seems to mark the course of an old river bed. It has a lateral extent of about 350 yards, passing into fine buff-coloured silt free from bitumen. The conglomerate was found to contain numerous bones, both mammal and bird, and thin-shelled freshwater gasteropods all firmly cemented in the bitumen. The bones, unfortunately, were too friable to collect, but I was fortunate in finding a good specimen of a tooth* which I have identified as belonging to the three-toed horse, Hipparion gracile, Kaup. It corresponds exactly with specimens collected by Polak from Maragheh, in Northern Persia, which I have examined in the Vienna Natural History Museum. H. gracile is a valuable zone fossil throughout Europe and Western Asia, so these Bakhtiari beds may now confidently be regarded as of Lower Pliocene (Pontian) age. This is the first fossil evidence of the age of this series to be found in South-Western Persia.

It is not possible to locate the position of the seepages which supplied the bitumen for this deposit, but it was probably somewhere to the north-east. The thick, partially inspissated, oil must have been carried into the valley by a stream, and, if the water periodically ceased to flow, this thick oil would be left to form swamps in the river bed. Such bones, teeth, shells, etc., which happened to fall or to be carried into this sticky swamp were firmly embedded, and so preserved from their normal fate of being ground to powder among the boulders of the river bed. There is every reason to expect that the plains at this period abounded in wild life, but it is only under exceptional circumstances that their remains can have been preserved.

* Specimen now in the Natural History Museum, South Kensington.

Further to the north-east on the flank of the Ableh anticline there are further occurrences of detrital bitumen in the Lower Bakhtiari conglomerates, in this case at about 200 feet above the base of that group. In the case of Khadda Sur, the bitumen horizon has been estimated by Mr. G. W. Halse, who is the original discoverer of the occurrence, to be about 2,200 feet above the base of the Bakhtiari series, which here overlies the Upper Fars with an angular discordance.

Fuller's Earth and its Uses in the Petroleum Industry.*

By A. Rauch, A.R.C.S., B.Sc., D.I.C. (Student Member).

The main object of this paper is to draw attention to the very important and useful properties of fuller's earth, a substance which is apparently very little used in the petroleum industry of Rumania. The American and British petroleum industries use fuller's earth and other similar materials on a very extensive scale and frequently to great advantage, and in addition it should be realised that its use as a decolourising and deodorising medium in the "vegetable and animal oil" industry is very considerable.

Details of the preparation of fuller's earth for use in the oil industry have been kept secret by the manufacturers, and only a few facts about its revivification are known.

The colour of crude fuller's earth varies considerably, but when refined and ready for use it is invariably cream coloured. On heating the earth on an ordinary sand bath in the laboratory, its colour becomes darker and when the temperature reaches approximately 300° C. a sudden transition to a greyish tint is observed. On raising the temperature still further, the colour gradually turns brown, but beyond 450° C. no further change in colour occurs. If the earth is then allowed to cool, its colour becomes light brown, but a somewhat darker shade than the original colour. Its specific gravity varies between 1·75 and 2·5.

As would be expected, the chemical composition of fuller's earth varies very much, it being mainly a mixture of aluminium silicate and iron oxide. The following is an analysis of a sample recently tested by the author :—

	Per cent.
Silica	56·7
Alumina	17·8
Iron oxide	3·1
Lime	3·2
Magnesia	1·2
Alkalies	0·3
Combined water	11·0
Moisture	6·5
Total	99·8

* Précis of paper read before the Rumanian Branch of the Institution at Ploesti on December 30th, 1926.

Fuller's earth has some very interesting properties, of which the most important for the petroleum industry is its absorbing power, use of which is made in the bleaching of oils. If an aqueous solution of an indicator or a dye, as for instance methyl orange or methylene blue, be filtered through fuller's earth, the latter absorbs the colouring matter, and a colourless filtrate is obtained. If filtration be continued until the earth becomes saturated with the dye, the filtrate becomes slightly coloured, the depth of the colour increasing as filtration proceeds.

Similarly, if a dark petroleum oil be filtered through fuller's earth, the first fractions of filtrate come through colourless, or very slightly coloured, the following fractions being progressively darker. No detailed work has as yet been published dealing with the changes in physical properties of petroleum oils on filtration through fuller's earth, but apparently the first fractions of the filtered oil have a lower density and viscosity than subsequent ones.

The mechanism of the decolourising action of fuller's earth is not yet fully understood. There are, however, several hypotheses, only three of which are at all probable. These three hypotheses account for the decolourising power of fuller's earth, firstly by absorption, secondly by adsorption, and thirdly by chemical action. Of these three, the second one, namely the adsorbing action, seems to be nearest to the truth. Absorption is defined as the penetration of the molecules of the absorbed substance into the actual body of the absorbing one. On the other hand, adsorption means the attachment of the adsorbed molecules on to the surface of the adsorbing medium. It has been stated that the grains of prepared fuller's earth have a great number of very minute pores or channels, and it has been suggested, this being the most likely explanation, that the molecules of the colouring matter in the oil, being much larger than the others, are held up in these pores or channels. There is another factor to be considered, and that is—why do the large molecules of the colouring matter enter the pores of the grains, and why do they not pass through the spaces between the grains of fuller's earth? In this connection it is possible that capillary attraction takes place, owing to the fineness of the pores of the grains; and that surface tension exerts an influence on the adsorbtion of the colouring matter, tending to fill up the pores. As to the chemical action accounting for the bleaching power of fuller's earth, there are two possibilities. They are, however, not very probable explanations, owing to the fact that the constituents of fuller's earth being present as silicates are not very reactive substances. The two possibilities are: firstly, that chemical action takes place between the grains of clay and the colouring matter, thus fixing the colouring substance next

to the grains, and secondly that a chemical action takes place, which changes the colouring matter into a colourless substance, under the catalytic action of the earth.

Fuller's earth is used in the petroleum industry in two ways: The oil is either filtered through a column of earth of coarse grade, or it is agitated mechanically or by air, with the necessary amount of fuller's earth to give the desired colour of oil. As to which of these two methods are used depends on certain factors—for, instance, the quality and viscosity of the oil to be treated, or the bleaching power and grade of the earth available. Benzine and kerosine fractions are usually refined by the so-called "contact system," while the lubricating oil fractions are refined by both filtration and contact systems.

In the contact system, the product, previously treated with sulphuric acid and soda, sulphuric acid only, or untreated, is agitated with fuller's earth, by air blowing in the case of gasoline and kerosine fractions, and by means of mechanical stirrers in the case of lubricating oils. The lubricating oils are not agitated by means of air because the colour of the oil tends to become darker owing to oxidation. In the case of benzine and kerosine fractions, the earth is allowed to settle out after agitations and is subsequently removed from the bottom of the agitator. This method of separating the earth from the oil involves large oil losses and therefore some refineries use suitable filter presses for the purpose. The lubricating oils are always separated from the clay (when used in the contact system) by means of a filter press.

The filtration method of refining oils requires a fairly coarse grade of clay, namely 15–30 or 30–60 mesh. The earth is placed on a perforated plate covered with a filter cloth and situated at the bottom of a cylindrical filter or percolator 6–10 ft. in diam. and 14–30 ft. in height. The oil is allowed to percolate through the earth, bleaching taking place during passage through the filter. From the latter, the oil runs to a receiving tank, from which samples are taken from time to time and tested until the contents of the tank have the required properties. The filtration of viscous oils is carried out at higher temperatures in order to facilitate percolation.

Fuller's earth, in addition to its decolorising properties, is capable of neutralising acid-treated oils.

This neutralising action of fuller's earth is very important, owing firstly to the great economy effected by eliminating the soda treatment and secondly to the fact that emulsification, which takes place with some lubricating oils when treated with soda, is prevented.

The advantage of the contact system over the filtration method is the saving of time, for whereas filtration occupies a considerable time, in the contact system the oil can be separated from the clay directly decolorisation is complete by means of filter pressing.

The advantages of the filtration method over the contact system are :—

1. Filter presses and mechanical power are not required.

2. Different coloured oils can be obtained from the same stock, while in the contact system the whole quantity of oil treated in one batch has the same colour.

3. Less handling of the earth is necessary, whereas in the contact system the earth must be removed from the filter cloth in order to be regenerated.

When the earth becomes inactive it is subjected to a naphtha washing followed by blowing with superheated steam, in order to remove the residual oil. It is then conveyed to a rotary kiln, where, after being heated to 500–600° C., the organic matter is burned off and the bleaching power practically restored completely.

A loss of 1–3 per cent. of earth occurs during the burning owing to the reduction of some of it to a very fine powder which is carried away by the draught. Again, the earth cannot always be regenerated completely, and thus the addition of fresh earth is required. If the earth could be revivified by a method which would not necessitate its removal from the percolator, a great economy could be realised, due to the elimination of roastings and conveying plant.

Fuller's earth can be completely regenerated by extracting the colouring matter which it has adsorbed from the oil, by means of suitable solvents, but as far as the author knows, no use has been made of this method on a commercial scale.

Suspensions of fuller's earth in distilled water frequently show an acid reaction towards litmus or phenolphthalein and the acidity can be titrated with N/10 caustic soda solution. By subjecting about 50 gms. of fuller's earth to dry distillation, a few drops of a colourless liquid can be obtained, which also have an acid reaction. It has been found that as a general rule the earths showing an acid reaction have greater bleaching properties than those which do not show this reaction. The bleaching power, however, is not proportional to the acidity.

When a suspension of fuller's earth showing a high acidity is subjected to the action of an electric current, the grains of earth migrate to the positive electrode, as if they were negatively charged.

The polymerising action of fuller's earth on unsaturated organic compounds was noted by Gurvitch when extracting with ether the colouring matter adsorbed by the earth from an oil. Investigation

showed that on mixing freshly rectified amylene (boiling point 39–40° C.) with an equal weight of dehydrated fuller's earth, a considerable rise in temperature occurred. After standing for two days, about 65 per cent. of polymerised products (boiling point above 100° C.) were obtained which consisted mainly of diamylene. Pinene treated with 5 per cent. of fuller's earth caused vigorous ebullition of the liquid and 6–7 per cent. of camphene was obtained. A later investigator did not obtain any camphene, but noticed the presence of dipinene and other polyterpenes.

If freshly heated fuller's earth be examined through a microscope, the grains of earth appear as white translucent masses with dark brown centres, while an exhausted grain appears completely black, as if impregnated with some dark substance.

The following facts must be borne in mind when using the filtration method :—

1. The longer the column of earth, the better the bleach and the lighter the colour of the oil.

2. The coarser the earth, the more rapid the flow and the poorer the bleach.

3. The finer the earth, the larger the surface of contact and the better the bleach.

4. The higher the temperature, the faster the flow and the poorer the bleach.

5. The higher the temperature, the less viscuous the oil, the more intimate the contact and the better the bleach.

It can be seen from points 4 and 5 that higher temperature has opposite effects on the bleaching of an oil. As a corollary of the above five facts, filtration should take place at the lowest temperature and with the finest grain of earth commensurate with speed of filtration.

Fuller's earth has also deodorising properties, *i.e.*, it adsorbs the strongly smelling compounds from petroleum oils.

A method has been developed in recent years which consists of deodorising cracked benzine distillates, by means of the deodorising and polymerising power of fuller's earth. It consists of passing the vapour of cracked benzine distillate over layers of fuller's earth maintained at a temperature higher than the boiling point of the distillate. It is claimed that the issuing vapours are completely deodorised owing probably to the fact that the strongly smelling unsaturated and sulphur compounds have been partly polymerised and partly adsorbed by the fuller's earth. The high boiling polymerised products can be drawn off from the bottom of the layers of fuller's earth.

In the vegetable and animal oils industry, great use is also made of the decolorising power of fuller's earth. Some earths have the

peculiar property of accelerating oxidation of the edible oils, thus imparting to some of them a rancid taste. Sometimes when filter presses in which fuller's earth has been filtered from an edible oil, are opened to air, they burst into flame, owing probably to very rapid oxidation when coming to contact with the atmosphere.

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Development of the Utilisation of the Fields Gas at Maidan-I-Naftun.*

THIS paper dealt with the underlying principles of the exploitation of natural gas as applied to the particular case of the gas of the S. Persia Oil Fields.

From the point of view of continuity and invariability of supply a study of the gas/oil relationship is of primary importance. Prognostication of supply on this basis requires decision as to the meaning of the terms "Gas" and "Oil" in determining the solubility constant and observations of the gas/oil ratio. These terms are best fixed arbitrarily. Moreover, it is necessary to form an opinion of the applicability of the gas laws to the system hydrocarbon gas/hydrocarbon liquid. The partial pressures of the chief constituents of the gas vary from 169 lbs. per sq. in. for methane to 28 lbs. per sq. in. for pentane. On the grounds of the non-associating character of the lower hydrocarbons and their chemical inertness it is considered that under the conditions which apply the deviation from Henry's Law will only be of the order of 15–25 per cent.

From a physico-chemical consideration of the gas/oil system it is possible to control the gasoline content of the separated gas, since there is an economic pressure of separation, an economic temperature of separation, and an economic vapour pressure of the recovered liquefiable constituents.

The choice of process for recovery of gasoline is made on the basis of gasoline content, range of efficiency, specificity and costs. The oil absorption process has been adopted.

The fundamental principles as determined by the applicability of the gas laws are summed up as follows :—

The size of plant is dependent on the volume of gas and, since the effective partial pressures determine the solubility, is independent of the gasoline content; despite the relative masses and specific heats and the low pressure used, cooling of the gas is of equal importance to the cooling of the oil, because of the high atmospheric temperatures encountered; low pressures of absorption are used because wide distribution of the stripped gas does not come into consideration. The limits of usefulness of the stripping oil are set

* Précis of paper read before Persian Branch of the Institution at Aberdeen. Received April 13, 1927.

when its vapour pressure equals the partial pressure of the recoverable constituents of the gas. A narrow range of products only is available from the crude oil for this purpose. As long as the system is counterflow type the actual design of the absorbers is of relatively little importance. The oil capacity is determined largely by the heat of solution, and the rate of flow by the yield and stability of the product desired.

The type of plant adopted and its performance was described.

Thermo Dynamics of Oil Refining as Bearing on Design of Plant.*

THE importance of heat and heat conservation in the operating and economy of an oil refinery is generally acknowledged, but the necessity for a complete and co-ordinated understanding of the reactions and operations depending upon the effects of heat and pressure have not been sufficiently appreciated.

The chemical and treatment side of oil refining receives the vast amount of attention commensurate with its importance; but the laws and relations of thermo dynamics and physics and their special bearing on distillation deserve greater attention and study.

The application of these laws to the design and operation of modern heat exchangers, coolers and condensers was touched upon and the importance of further systematic research and study emphasized. The general principles of fractional distillation were outlined, and their special application to a modern pipe still bench fitted with fractionating columns and tubular condensers was considered in some detail by following a typical flow diagram. A brief outline was given of the Sharple's process for the dewaxing of amorphous distillate by means of slow cooling and subsequent centrifuging, and of high vacuum distillation plants for lubricating oils.

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* Précis of paper read before Persian Branch of the Institution at Aberdeen. Received April 13, 1927.

Contributed discussion on Mr. A. Beeby Thompson's paper on "The Significance of Surface Oil Indications."*

The following has been received from **Dr. Donald C. Barton** :—

The Indications of the Oilfields in the Mid-Continent and Gulf Coastal Plain of the United States.

The Mid-Continent and the Gulf Coastal Plain oilfields in the United States were mentioned a considerable number of times in Mr. A. Beeby Thompson's interesting paper on "Surface Oil Indications" and the ensuing discussion. May I add the following more detailed information regarding the indications which led to the discovery of most of the oilfields in Arkansas, Louisiana, Oklahoma and Texas. The data on the older oilfields and Oklahoma were culled from the literature. The date on Arkansas, North Louisiana and the Texas Pennsylvanian-Ordovician oilfields are mostly from conversation with geologists familiar with the development of those oilfields and partly from the literature. The writer is personally familiar with the Gulf Coast, the Texas fault-line and West Texas Permian oilfield districts in the past few years.

Tertiary Oilfields of the Texas-Louisiana Gulf Coast Salt Dome Area.

Among the larger and more prolific oilfields, the indications which led to the discovery of the oil were :—

Gas seeps and faint oil seeps : at the Batson ; (also asphalt at the surface) Sour Lake ; South Liberty-Dayton ; also (H_2S water and sour water) Saratoga oilfields.

Gas seeps and paraffin dirt : at the Goose Creek† and Orange† oilfields.

Gas seeps and salt dome mound : at the Jennings, West Columbia ; (also sour water and show of oil in 20-ft. water wells) Vinton ; (also incrustation of native sulphur probably reduced from H_2S) Spindletop ; and (mound erosional) Humble oilfields.

Salt dome mound without other indications : at the Hull oilfield.

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* *Journ. Inst. Petr. Techn.*, 1926, **12**, 59, pp. 603-634.

† Oilfields not associated with salt domes.

Among the moderate-sized oilfields, the indication which led to the discovery of the oil were :—

Gas seeps : at the Markham, North Dayton, Westlake† oilfields.

Gas seeps and paraffin dirt : at the Edgerly† oilfield.

Salt dome mound and gas seeps : at the Anse la Butte, and (gas in 65-ft. well) Barbers' Hill oilfield.

H_2S water in water wells>50 ft. deep : at the Big Creek and Boling oilfields.

Salt dome mound : at the Blue Ridge, and (also " sour " dirt) Damon Mound.

Among the very small-sized oilfields, where only a very few commercially profitable wells have been completed and whose total production has been small, the indications which led to the discovery of the oil were :—

Salt dome mound : at the Big Hill, Hoskins Mound, Matagorda, and (also an outcrop of limestone cap rock) Pine Prairie oilfields.

Gas seeps : at the Hockley, and (in an irrigation water well, also a mound not a salt dome mound) Welsh† oilfield.

Gas seeps and paraffin dirt : at the New Iberia oilfield.

Salt dome mound, gas seeps and saline springs : at the High Island oilfield.

Among the very recently-discovered oilfields, whose size is not yet known, the following indications led to the discovery of the oil :—

Discovery of a salt dome by geophysical methods : at the Fannet, Orchard, Long Point and Starks oilfields.

H_2S water in water well 50>ft. deep and the discovery of a salt dome by geophysical methods : at the Nash oilfield.

Gas seeps, paraffin dirt and the discovery of a salt dome by geophysical methods ; at the Lake Fausse Oilfield.

Gas seeps ; at the Sweet Lake oilfield†.

Gas in water well and pyritisation at the surface ; at the Bellville† gasfield.

Oil seep and gas show and ? sour dirt : at the Sulphur oilfield.

No commercial oil well has been completed on any one of the following salt domes :—Allen, Bryan Heights, Clements, Davis Hill, Hackberry, Hawkinsville, Jefferson Island, Avery Island, Weeks Island, Cote Blanche, Belle Isle, Section 28, Bayon Bouillon, and there are four and perhaps five salt domes recently discovered by geophysical methods which have not been drilled.

A few gas seeps have been drilled unsuccessfully within the coastal salt dome area proper ; a small gas seep without paraffin dirt at Bayou Arsene, near Lake Charles, Louisiana ; a small gas seep with a fair but small accompanying bed of paraffin dirt at St. Martinsville, Louisiana ; several very small gas seeps and very small poor beds

of paraffin dirt around Spanish Lake, Louisiana. Some of the as yet unproductive salt domes are marked at the surface by gas seeps and paraffin dirt. East, north and south-west of the coastal salt dome area proper there are good gas seeps, and, except at the south-west, good beds of paraffin dirt, which seem to be associated with gas and not oil.

The paraffin dirt bed at St. Martinsville is the only even fairly good occurrence of paraffin dirt within the area of the coastal salt domes, known to the writer to have been drilled without the discovery of oil, a salt dome or gas. Although when even fairly well developed paraffin dirt has a very distinct individuality to those who have come to know it, the uninitiated mistake many things for it and many wells have been drilled, mostly by the less responsible operators, on the basis of a mistaken identification of paraffin dirt. In connection with the assertion that has been made several times recently that many geologists familiar with the Gulf Coast have come to doubt the significance of paraffin dirt as an indication of oil, the writer requested two past presidents of the American Association of Petroleum Geologists, who are themselves specialists on the Gulf Coast, to select the ten geologists most competent as authorities on the Gulf Coast. Of the following list of ten names seven were first choice of both men and three were first choice of one and second choice of the other: Barton, De Golyer, Duessen, Donoghue, Dumble, Garrett, Goodrich, Lee Hager, Henniger, Pratt. Expressions of belief were then requested of them in regard to the following questions with the following results :—

Questions.	Answer: Yes.	Qualified Yes.	No.
1. The significance of paraffin dirt as an indication of petroleum deposits is the same as that of a seep of natural gas	5	2	0
2. From Anse La Butte west in the area of the coastal group of salt domes (*i.e.*, the area of the coastal salt dome oilfields not in the swampy back bottoms and delta of the Mississippi River and enclosing all but two, small oilfields), paraffin dirt is a reasonably reliable indication of oil deposits	6	1	0
3. From Anse La Butte west in the area of the coastal group of salt domes, do you know of any authentic, distinct beds of paraffin dirt that are not on salt domes or associated with oilfields?	0	0	6 (Questionable bed, 1)

No replies to the questionnaire were received from three of the ten men.

Many mounds have been drilled unsuccessfully in the hope that they might be salt dome mounds. A few of the mounds simulated salt dome mounds, but most of the mounds could easily be recognised

by a physiographer as by erosion mounds, beach ridges, portion of an ancient natural levee, sand dune, etc.

"Sulphur water"—that is, water carrying H_2S in solution has led to the discovery of a considerable number of salt domes and oilfields, but is a very treacherous indication and a very great many unsuccessful tests have been drilled at sulphur water seeps. Hydrogen sulphide is generated in many marshy places and at the surface it is impossible to differentiate between sulphur waters bearing H_2S of surface origin from those bearing H_2S of deep-seated origin. A considerable number of unsuccessful tests, however, have been drilled where the sulphur water came from >50 ft. wells in dry upland areas.

Oil shows in three places at least have been drilled unsuccessfully. In each place droplets of "live" oil came up with the water from wells 40-300 ft. deep.

Surface indications are no longer considered as important in the Gulf Coast salt dome area and little search is made for them. The present-day search for new oilfields is almost entirely by reconnaissance with geophysical instruments; one oil company has spent some three million dollars in the past three years in the operation of geophysical surveys.

Not all of the salt domes are commercially productive as yet, but it is very difficult to determine when a salt dome is condemned. On account of the small area of the salt dome oilfields a great many unsuccessful wildcats commonly have to be drilled before the productive area of a known salt dome is located. The discovery well at West Columbia was the 41st well drilled within an area of three square miles. Most of the wells, however, were less than 2000 ft. deep. The discovery well at Pierce Junction was the 55th well drilled within an area of three square miles, and of the first 54 wells some half went to a depth of at least 3000 ft. At Spindletop, where the 2000-ft. contour on the salt has a diameter of 6000 ft., five deep tests (3700, 4100, 5400, 4700, 3950 ft. deep respectively) were drilled within 1000 ft. of the 2000-ft. contour without discovering the very prolific deep sand pool, from which some 1,500,000 barrels of oil has been produced in the past year. The writer has calculated that for an average salt dome 1 mile in diameter, 10 wells 1000 to 1800 ft. deep, 10 wells 3000 to 4000 ft. deep, and 10 wells 6000 ft. deep are necessary to condemn the salt dome with a probability of 80 per cent.

Cretaceous Oilfields.

Fault Line Oilfields of Texas.—Grossbeck-Powell district. The discovery of oil in that district was due to the finding of oil in a 1027-ft. water well at Corsicana, which led to the subsequence

discovery of numerous shallow oil and gas fields. The much later discoveries of the prolific Mexia, Wortham and Powell deep-sand oilfields were based on structural geology.

Lytton Springs and Luling, discovered on the basis of surface geologic structure.

San Antonio district (Somerset), shallow oil district, discovered by the finding of oil in a 500-ft. water well.

Louisiana and Arkansas.—Caddo oilfield, discovered on the basis of gas seeps in and around Caddo Lake.

The prolific Homer, Haynesville and Eldorado oilfields, discovered on the basis of surface geology.

The prolific Smackover oilfield, discovered on the basis of dubious geology or accident.

Monroe, a very large and extensive gasfield, discovered on account of the finding of gas in a 1300 ft. water well.

Bellevue, discovered on the basis of geologic structure.

Red River-De Soto oilfield, discovered on the basis of surface geologic structure and the finding of gas in a 800-ft. well.

Permian Oilfields of Texas and New Mexico.

Big Lake oilfield, discovered by accident; the transportation broke down and the well was drilled at that point instead of at the intended location which has since been shown to be several miles from the oilfield.

McCamey-Hurdle oilfields, discovered on the basis of surface geology.

Artesia oilfield, discovered on the basis of surface geology.

Panhandle oilfields, discovered on the basis of surface geology.

Small, shallow oilfields of the Obney district, discovered on the basis of surface geology and much chance.

Pennsylvanian-Ordovician Oilfields of Central to North Texas.

Ranger, South Bend oilfields, discovered on the basis of surface structure; the writer understands on less definite authority that most of the fields in that area were discovered on the basis of surface geology or accident

Oklahoma.*

Permian, Pennsylvanian and Ordovician Oilfields.—Oil seepages, according to Powers, had less to do with the oil development in Oklahoma than in almost any other part of the world; the oil

* Sidney Powers, Petroleum Geology in Oklahoma. *Oklahoma Geol. Surv. Bull., No.* 40-b, 1926.

seepages are practically confined to the outcrop of the "Bartlesville" sand in the adjacent portion of south-western Missouri and to the outcrop of certain sandstones in Southern Oklahoma. The Wheeler oilfield was discovered because of the prolific seepages there.

Surface anticlines or anticlinal noses mapped by the geologists led to the discovery of the Billings, Blackwell, Boston, Boynton, Brock, Cement, Cromwell, Duncan, Fox, Garber, Hewitt, Ingalis, Lyons, Mannford, March, Mashan, Newkirk, Quin, Ripley, Robberson, Seminole, Stroud, Tonkawa, Velma, Walters, Yale and Youngstown oilfields. The Cushing oilfield is on a surface anticline, but was discovered before the days of oil geology in Oklahoma.

Geologic structure worked out by diamond core drills led to the discovery of Tonkawa (in part), North and South Braman, Hubbard, Mehan and Thames oilfields.

Chance drilling led to the discovery of the Cushing, Ponca City, Papoose and Wewoka oilfields and many others, especially small, shallow pools in Washington, Nowata, Tulsa, Muskogee and Okmulgee Counties.

Conclusion.

The most striking characteristic of the several major oil provinces of Arkansas, Louisiana, Oklahoma and Texas is the faintness of the surface indications of the oil and gas. The oil seepages are few. In Texas, Louisiana, and Arkansas the oil seepages are inconspicuous and the outcrops of the productive horizons are not marked by them. The gas seeps which led to the discovery of so many of the coastal oilfields for the most part are inconspicuous; and the really conspicuous gas seeps, in the area east of Bayou Teche, Louisiana, and in the zone through Sabinetown and Grimes County, Texas, however, have not led to the discovery, as yet, of commercial oilfields. Some of the anticlines and anticlinal noses which led to the discovery of oilfields in Oklahoma can be recognised easily on reconnaissance on account of the coincidence of open country and hills capped by resistent limestones or sandstones, but most of them can be recognised only by careful detailed surveying of key beds with the planetable and alidade. In the area of the Cretaceous and Permian oilfields of Texas, Louisiana and Arkansas the surface structure indicative of the oilfields below is extremely inconspicuous. At Mexia the presence of faulting might be recognised on reconnaissance, and at Luling the fault is clearly exposed only at one point, but otherwise the surface structure of the fault-line oilfields can be recognised only by very careful and detailed geological work involving careful stratigraphic mapping. In Louisiana and Arkansas the surface structure of the oilfields can

be worked out only by careful and intensive geologic work, and even then in most cases is more or less dubious. In the Texas Panhandle the buried granite ridge is partly indicated by surface structure, but the oil is found only in flank sands and is several miles off from the centres of the surface domes. Elsewhere in the West Texas Permian basin the surface expression of the oilfield structures is extemely indefinite or wanting.

If Arkansas, Louisiana, Oklahoma and Texas were in a moderately wild, wooded foreign country a fairly detailed reconnaissance survey would probably result in the condemnation of the area as not showing sufficient indications of oil or structure to warrant expensive exploration. If exploration were started on some of the few oil or gas seeps, the probability would be more than 90 per cent. that the results of the exploration would not be commercially successful. The prolific Cretaceous oilfields of Texas, Louisiana and Arkansas would not be discovered by the most detailed mapping warranted by a wild country not known to be petroliferous, and if the salt domes of the Gulf Coast were recognised the difficulty of finding the small though prolific oilfields is so great that so many great domes might have to be drilled before the discovery of oil in commercial quantity that the coastal salt dome area would be considered condemned before oil was discovered.

Contributed Discussion on Mr. E. Parsons' Paper on "The Structure and Stratigraphy of the North-West Indian Oilfields."*

The following has been received from **Mr. E. S. Pinfold** :—

Mr. Parsons' main thesis is that the oil of North West India has its origin in the basal beds of the nummulitic limestones and that it reaches the surface as seepages by movement along overthrusts. A careful perusal of his paper fails to reveal any relevant evidence in support of his contention.

The horizon to which Mr. Parsons attributes the oil is exposed over a very wide area within the admitted "oil-belt" and nowhere is it known to be oil-bearing. Of the two localities in which the oil-seepages might be regarded as of this horizon, Kundal and Chak Dalla, the oil-bearing rocks are Mesozoic (they have yielded belemnites) at the former and some distance above the base of the nummulitic limestone at the latter.

Mr. Parsons' paper would have been more convincing if he had disposed of the direct negative evidence against his thesis. For

* *Jour. Inst. Petr. Techn.*, 1926, **12**, 58, pp. 439-505.

example, in the Trans-Indus Salt Range directly between Kundal and Panoba the rocks which he regards as the oil source rocks are mined for coal along a large pitching anticlinal near Mulla Khel —a locality frequently referred to in Mr. Parsons' paper. In these mines no trace of oil has been encountered, whereas only some ten miles further south (actually a few hundred feet higher in the succession on the same structure) there is a considerable oil seepage in the basal Siwalik beds.

A more striking instance is furnished by a test well drilled for oil some four or five years ago near Kabakki in the Cis-Indus Salt Range. This well was located at the summit of a large perfect dome in the Salt Range nummulitic limestone near the centre of a group of seepages including the largest individual seepage in the Cis-Indus Punjab. This well passed completely through the nummulitic limestones into older rocks without getting any trace of oil. If Mr. Parsons' contemplates further testing of this same horizon (as appears probable from his paper) this area should have his careful attention.

It would take too long to discuss all the controversial points raised by Mr. Parsons, but two other passages in his paper cannot be allowed to pass without comment :—

On page 498 Mr. Parsons claims the presence of a longitudinal fault at Khaur as "strongly confirmatory" of his views. I am strongly at variance with Mr. Parsons over this view. The distribution of oil in the Khaur field has proved to be very irregular, but there has been no evidence to indicate that this fault has played any important part in the upward migration of the oil to its present reservoirs. On the contrary, the wells drilled nearest to the fault have, up to the present, given definitely inferior results to wells drilled further away from it.

Towards the end of his paper Mr. Parsons states, somewhat gratuitously, "Pinfold undoubtedly supports the view expressed by Griesbach who was struck by the large foraminiferal (Rummulitic) life in the rocks and attributed the origin of the oil to the abundance of those organisms." On one occasion only did I mention nummulites in connection with the origin of the oil in North West India and then I wrote* :—"The most abundant fossils in the Lower Tertiary rocks are nummulites and some beds of considerable thickness are made up entirely of nummulite tests. Such beds, however, are not oil-bearing. Neither the massive nummulitic limestones nor the nummulite shales contain original oil and it is improbable that nummulites contributed in any way to the formation of the oil."

* *Jour. As. Soc. Bengal*, 1918, N. S. XIV., p. c/xxxii.

REVIEW.

CHEMICAL ENGINEERING AND CHEMICAL CATALOGUE. Edited by D. M. Newitt. 3rd Edition. Pp. 404. London: Leonard Hill, 1927. 15s.

In this edition, the Classified Index of Chemicals and Chemical Plant occupies 101 pages, being preceded by 172 pages of catalogue matter in the form of manufacturers' advertisements. An Index to Industrial Applications is included and forms a very useful guide to the chemicals and plant likely to be of use in various industrial processes. The section on Tables and Data contains a considerable amount of information in a convenient form for quick reference. The work concludes with a section on Scientific and Technical books. This section is in two parts, the first being a subject index with references to authors' names, under which are found, in the second part, particulars of the books and in many cases a list of chapter headings.

This edition of the book shows a considerable advance over the previous editions and should prove useful in the chemical and allied industries.

GEORGE SELL.

BOOKS RECEIVED.

LOW TEMPERATURE CARBONISATION. C. H. Lander and J. Fraser Shaw. Fuel Research Technical Paper, No. 17. H.M. Stationery Office, 1927. 6d. net.

A preliminary account of the construction and behaviour of the latest vertical cast-iron retorts erected at the Fuel Research Station, Greenwich.

METHODS OF ANALYSIS OF COAL. Physical and Chemical Survey of the National Coal Resources, No. 7. H.M. Stationery Office, 1927. 9d. net.

A report by the Sampling and Analysis of Coal Committee of the Fuel Research Board on the methods of analysis adopted by the Department of Scientific and Industrial Research in its work on coal.

AN INVESTIGATION OF THE CAKING POWER OF COAL. J. T. Burdekin. Physical and Chemical Survey of the National Coal Resources, No. 8. H.M. Stationery Office, 1927. 1s. net.

In order to obtain fuller information as to the caking qualities of coal, investigations have been carried out with various types of apparatus. The one described involves heating the coal, mixed with calcined anthracite, at a standard rate, and then determining the crushing strength of the cokes.

THE PRIMARY DECOMPOSITION OF COAL. 1. THE TEMPERATURE OF INITIAL DECOMPOSITION. J. G. King and R. E. Willgress. H.M. Stationery Office, 1927. 9d. net.

The paper is the first of a new series of reports on laboratory investigations into the behaviour of coal on heating and on the products of distillation or carbonisation. The investigations are continuing and further reports will be issued in due course.

DESCRIPTIVE BIBLIOGRAPHY ON OIL AND FLUID FLOW AND HEAT TRANSFER IN PIPES. Joe B. Butler. *Technical Series Bulletin*, Missouri School of Mines.

This bulletin of 62 pages lists and describes 370 references to published articles and books. The references are arranged chronologically as to year of publication, are fully cross-referenced, and are indexed as to subject, author and periodical. A short article on the flow of oil in pipes gives formulas, data and procedure in solving problems.

All articles with data on friction loss and heat transfer in oil flow are included. Of the articles on flow and heat transfer in pipes of water, air, steam and gases, only those with data pertaining to fluids in general are listed. Articles on critical velocity, viscosity and viscosimetry are included if they have applications to oil or fluid flow in pipes.

In 1914, Stanton and Pannell experimentally established for fluid flow in pipes that the friction factor in the ordinary hydraulic formulas is a function of the ratio of the inside diameter of the pipe times the average velocity of flow times the specific gravity of the fluid divided by the absolute viscosity of the fluid. Curves showing this relation over both the streamline and turbulent regimes of flow are plotted from experimental data on water, air, oil and steam. The author lists 51 references having data or curves applicable to oil over both regimes of flow.

Copies of this bulletin may be obtained by writing to the Librarian of the Missouri School of Mines, Rollo, Missouri, or to the author.

ERRATA.

In figure 2 of "Factors Affecting Internal Combustion," Journal 60, p. 110, the photograph on the left has been reversed.